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# SOME THEOREMS IN OPERATIONAL CALCULUS

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We know in operational calculus that if the 'image' $f(p)$ of an 'original' function $h(x)$ can be broken up into 'images' $f_1(p), f_2(p), \ldots f_n(p)$, etc., of different 'original' functions $h_1(x), h_2(x), \ldots h_n(x)$ and if

$$f(p) = \frac{1}{p^{n-1}} f_1(p) f_2(p) \ldots f_n(p)$$

then $h(x)$ can be related with $h_1(x), h_2(x) \ldots h_n(x)$ by means of the relation $h(x) =$

$$\int\int \ldots \int h_1(t_1)\, h_2(t_2) \ldots h_{n-1}(t_{n-1})\, h_n[x - t_1 - t_2 \ldots - t_{n-1}]\, dt_1\, dt_2 \ldots dt_{n-1}$$

where $t_1, t_2, \ldots t_{n-1}$ are all $\geqslant 0$ and

$$t_1 + t_2 + t_3 + \ldots + t_{n-1} \leqslant x.$$

The product theorem of the operational calculus is only a particular case of this. But so far as is known, no attempt has yet been made to investigate the problem of establishing relationship between $f(p)$ and $g(t)$, if the 'original' $h(x)$ of the operational 'image' $f(p)$, is itself an 'image' or is a part of the 'image' of another 'original' function $g(t)$. We have solved this problem in this paper for certain suitable forms of the 'image' of $g(t)$. We have established some theorems which are found useful in deducing new properties of known functions occurring in mathematical physics and in obtaining new operational representations. For the justification of the change in the order of integration the test due to de la Valle's Poussin, as given by Bromwich[1] is used. For the investigation of theorems I–III in articles I and II, $f(x, y)$ is either of the type

(i) $\exp\left[-px - \frac{y}{x}\right] x^{-s-1}\, g(y)$ $\quad p$ +ve

(ii) $\exp[-(p+y)x]\, x^{s+1}\, g(y)$ $\quad$ R $(s) > -2$ and $p$ +ve.

Hence it is sufficient for the inversion of the order of integration that $g(y)$ should be bounded and integrable in $y \geqslant 0$ and

$$\int_0^y |g(y)|\, dy \text{ is convergent.}$$

The relation $f(p) \doteqdot h(x)$ means that the functions $f(p)$ and $h(x)$ are 'operationally' related, *i.e.*,

$$f(p) = p \int_0^\infty e^{-px} h(x)\, dx. \qquad \mathrm{R}(p) > 0.$$

the integral being supposed convergent, and $f(p)$ is called the 'image' of the 'original' function $h(x)$. In what follows we will use two theorems of operational calculus and they will be denoted as $\mathrm{F}_1$ and $\mathrm{F}_2$ *viz.*,

If $h(x) \doteqdot f(p)$

then

(i) $h(ax) \doteqdot f\left(\frac{p}{a}\right)$ a constant $> 0$ $\quad (\mathrm{F}_1)$

(ii) $e^{-\lambda x} h(x) \doteqdot \frac{p}{p+\lambda} f(p+\lambda)$ $\quad (\mathrm{F}_2)$.

I. Now if $f(p) \doteqdot h(x)$ and $h(p)\,\phi(p) \doteqdot g(x)$, then by definition we get

$$f(p) = p \int_0^\infty e^{-ps} h(s)\, ds \qquad p > 0$$

and

$$h(s)\,\phi(s) = s \int_0^\infty e^{-st} g(t)\, dt \qquad s > 0$$

both integrals being convergent. Hence

$$f(p) = p \int_0^\infty g(t) \left[ \int_0^\infty e^{-(p+t)s} \frac{s}{\phi(s)}\, ds \right] dt \qquad (1\cdot1)$$

after substituting the value of $h(s)$ and then changing the order of integration. If we assume in $(1\cdot1)$ $\phi(s) = s^{-m}$ we will have by using the integral

$$\int_0^\infty e^{-(p+t)s} s^{m+1}\, ds = \frac{\Gamma(m+2)}{(p+t)^{m+2}}, \quad \mathrm{R}(m) > -2,$$

$p + t$ being positive $\qquad (1\cdot2)$

THEOREM I.— If $f(p) \doteqdot h(x)$ and $\frac{1}{p^m} h(p) \doteqdot g(x)$, then

$$f(p) = \Gamma(m+2)\, p \int_0^\infty \frac{g(t)}{(p+t)^{m+2}}\, dt \quad \mathrm{R}(m) > -2$$

$p$ being positive and $g(t)$ satisfying the conditions given in the introduction. As an example on this theorem, consider

$$g(x) = x^{\frac{n}{2}} \mathrm{J}_n(a\sqrt{x}) \qquad \mathrm{R}(n) > -1.$$

By applying $F_1$ to the operational representation[2]

$$x^{\frac{n}{2}} J_n(2\sqrt{x}) \doteqdot p^{-n} e^{-\frac{1}{p}} \qquad R(n) > -1$$

we get

$$\begin{aligned} x^{\frac{n}{2}} Jn(a\sqrt{x}) &= g(x) \\ &\doteqdot \left(\frac{a}{2}\right)^n p^{-n} e^{\frac{a^2}{4p}} \\ &= \left(\frac{a}{2}\right)^n p^{-\mu+1} \cdot e^{-\frac{a^2}{4p}} p^{\mu-n-1} \\ &= \phi(p) \cdot h(p). \end{aligned}$$

Again from the integral[3]

$$\int_0^\infty e^{-2u-\frac{\omega^2}{4u}} u^{-s-1}\, du = 2^{\frac{1}{2}(3s+2)} \omega^{-s} K_s(\sqrt{2}\,\omega) \qquad (1\cdot3)$$

where $K_s$ is the Bessel function of the second kind and $R(\omega^2) > 0$, we get by the substitutions $\omega^2 = 4p$ and $u = \frac{1}{x}$, the operational representation

$$x^{s-1} e^{-\frac{1}{x}} \doteqdot 2p^{1-\frac{s}{2}} K_s(2\sqrt{p}) \quad R(p) > 0 \qquad (1\cdot4)$$

By applying $F_1$ to this we obtain

$$x^{s-1} e^{-\frac{a^2}{4x}} \doteqdot 2\left(\frac{a}{2}\right)^s p^{1-\frac{s}{2}} K_s(a\sqrt{p}) \quad R(p) > 0 \qquad (1\cdot5)$$

Hence

$$\begin{aligned} h(x) &= x^{\mu-n-1} e^{-\frac{a^2}{4x}} \\ &\doteqdot 2\left(\frac{a}{2}\right)^{\mu-n} p^{1-\frac{\mu-n}{2}} K_{\mu-n}(a\sqrt{p}) = f(p). \end{aligned}$$

Therefore by Theorem I proved just now we get after simplification

$$2\left(\frac{a}{2}\right)^\mu p^{\frac{1}{2}(n-\mu)} \frac{K_{\mu-n}(a\sqrt{p})}{\Gamma(\mu+1)} = \int_0^\infty \frac{x^{\frac{n}{2}} J_n(a\sqrt{x})}{(p+x)^{\mu+1}}\, dx \qquad (1\cdot6)$$

Changing $x$ into $x^2$ and $p$ into $p^2$ we get the well-known result*

$$\frac{1}{\Gamma(\mu+1)} \left(\frac{a}{2}\right)^\mu p^{n-\mu} K_{\mu-n}(ap) = \int_0^\infty \frac{x^{n+1} J_n(ax)}{(p^2+x^2)^{\mu+1}}\, dx$$

$$\begin{matrix} R(\mu) > -1 \\ 2R(\mu) + \frac{3}{2} > R(n) > -1 \\ R(p) > 0 \end{matrix}$$

* Walson, *Bessel Functions*, p. 434 (2).

As a second example on the theorem consider the operational representation

$$x^m \, \mathrm{T}_m^n(x) \doteqdot \frac{(1-p)^n}{\Gamma(n+1)\, p^{m+n}} \tag{1·7}$$

where $n$ is an integer and $\mathrm{R}(m+n) > 1-$. $\mathrm{T}_m^n(x)$ being Sonine's polynomial which is a generalization of the parabolic cylinder function. By applying $\mathrm{F}_2$ to (1·7) we get

$$\begin{aligned} g(x) &= e^{-x}\, x^m \cdot \mathrm{T}_m^n(x) \\ &\doteqdot \frac{(-)^n\, p^{n+\mu}}{\Gamma(n+1)\,(1+p)^{m+n+1}} \cdot \frac{1}{p^{\mu-1}} \\ &= h(p) \cdot \frac{1}{p^{\mu-1}}. \end{aligned}$$

Hence

$$h(x) = \frac{(-)^n}{\Gamma(n+1)} \cdot \frac{x^{n+\mu}}{(1+x)^{m+n+1}}$$

$f(p)$ the 'image' of $h(x)$ is the value of the integral

$$p \int_0^\infty \frac{(-)^n}{\Gamma(n+1)} \frac{x^{n+\mu}}{(1+x)^{m+n+1}} e^{-px}\, dx \qquad p>0$$

$$= \frac{(-)^n\, \Gamma(\mu+n+1)\, e^{\frac{1}{2}p}}{\Gamma(n+1)\, p^{\frac{1}{2}(\mu-m-1)}} \mathrm{W}_{-\frac{1}{2}(m+\mu+2n+1),\, \frac{1}{2}(\mu-m)}(p)$$

$$p>0,\ \mathrm{R}(\mu+n+1) \geqslant 0$$

obtained by using the substitution $px = t$ and the integral[1]

$$\mathrm{W}_{k,m}(z) = \frac{e^{-\frac{1}{2}z}\, z^k}{\Gamma(\frac{1}{2}-k+m)} \int_0^\infty e^{-t}\, t^{-k-\frac{1}{2}+m} \left(1+\frac{t}{z}\right)^{k-\frac{1}{2}+m} dt \tag{1·8}$$

$$\mathrm{R}(k-\tfrac{1}{2}-m) \leqslant 0$$

Therefore by applying the theorem investigated we get

$$\int_0^\infty \frac{e^{-t}\, t^m\, \mathrm{T}_m^n(t)}{(p+t)^{\mu+1}}\, dt =$$

$$\frac{(-)^n\, \Gamma(\mu+n+1)\, e^{\frac{1}{2}p}}{\Gamma(\mu+1)\,\Gamma(n+1)\, p^{\frac{1}{2}(\mu-m+1)}} \mathrm{W}_{-\frac{1}{2}(m+\mu+2n+1),\, \frac{1}{2}(\mu-m)}(p)$$

$$\mathrm{R}(\mu+1) > 0 \text{ and } \mathrm{R}(\mu+n+1) \geqslant 0.$$

If we put $p = a^2$ and $t = x^2$ we get

$$2\int_0^\infty \frac{e^{-x^2}\, x^{2m+1}\, \mathrm{T}_m^n(x^2)}{(a^2+x^2)^{\mu+1}}\, dx.$$

$$= \frac{(-)^n\, \Gamma(\mu+n+1)\, e^{\frac{1}{2}a^2}}{\Gamma(n+1)\,\Gamma(\mu+1)\, a^{\mu-m+1}} \mathrm{W}_{-\frac{1}{2}(m+\mu+2n+1),\, \frac{1}{2}(\mu-m)}(a^2) \tag{1·9}$$

$$\mathrm{R}(\mu+1) > 0,\ \mathrm{R}(\mu+n+1) \geqslant 0.$$

The particular cases of (1·9) for (i) $m = \frac{1}{2}$ and $\mu = 0$ and (ii) $m = -\frac{1}{2}$ and $\mu = 0$ yield results already obtained[5] as both Sonine's polynomial $T_m^n(x)$ and Whittaker's function $W_{k,m}(x)$ are connected with parabolic cylinder functions by well-known relations.

II. If $f(p) \doteqdot h(x)$ and $h\left(\frac{1}{p}\right)\phi\left(\frac{1}{p}\right) \doteqdot g(x)$ instead of $h(p)\,\phi(p) \doteqdot g(x)$ as assumed in the previous case, we get

$$f(p) = p\int_0^\infty g(t)\left[\int_0^\infty e^{-(px+\frac{t}{x}}\frac{1}{x\,\phi(x)}\,dx\right]dt \qquad p>0$$

This yields two interesting theorems if we take for $\phi(x)$

$$\text{(i)}\quad \frac{1}{\sqrt{x}} \qquad \text{or (ii)} \quad x^c$$

In the first case we get by using the integral

$$\int_0^\infty e^{-\left(px+\frac{t}{x}\right)}\,x^{-\frac{1}{2}}\,dx = \sqrt{\frac{\pi}{p}}\,e^{-2\sqrt{tp}} \tag{2·1}$$

the theorem: if $f(p) \doteqdot h(x)$ and $\sqrt{p}\,h\left(\frac{1}{p}\right) \doteqdot g(x)$, then

$$\frac{f(p)}{\sqrt{\pi p}} = \int_0^\infty e^{-2\sqrt{pt}}\,g(t)\,dt \qquad p>0$$

provided $g(t)$ satisfies the conditions already given and that the integral is convergent. If we change $p$ into $\frac{p^2}{4}$ and $t$ into $x^2$ and use the definition of the operational representation we can restate the above as

Theorem II:

If $f(p) \doteqdot h(x)$ and $\sqrt{p}\,h\left(\frac{1}{p}\right) \doteqdot g(x)$, then $\frac{1}{\sqrt{\pi}}f\left(\frac{p^2}{4}\right) \doteqdot x\,g\,(x^2)$, a theorem useful in getting new operational representations.

Let us now take the second value of $\phi(x)$ and use (1·3) with the substitution $px = 2u$, we get Theorem III:

If $f(p) \doteqdot h(x)$ and $\frac{1}{p^s}h\left(\frac{1}{p}\right) \doteqdot g(x)$, then

$$f(p) = 2p^{\frac{s}{2}+1}\int_0^\infty t^{-\frac{s}{2}}\,g(t)\,K_s(2\sqrt{pt})\,dt$$

provided $R(p) > 0$; $g(t)$ satisfying the conditions already given, $K_s$ representing Bessel function of the second kind.

We will now take some examples by way of application of the theorems investigated.

(i) Let $g(x) = x^{\frac{n}{2}} J_n(2\sqrt{x})$

$$\doteqdot p^{-n} e^{-\frac{1}{p}} \quad R(n) > -1$$

$$= p^{\frac{1}{2}} \cdot p^{-(n+\frac{1}{2})} e^{-\frac{1}{p}}$$

$$= \sqrt{p}\, h\left(\frac{1}{p}\right)$$

Therefore $h(x) = e^{-x} x^{n+\frac{1}{2}}$

$$\doteqdot \Gamma(n+\tfrac{3}{2}) \frac{p}{(1+p)^{n+\frac{3}{2}}}.$$

$$= f(p)$$

by applying $F_2$ to

$$x^n \doteqdot \frac{\Gamma(n+1)}{p^n}.$$

Therefore from Theorem II we get the operational representation

$$\frac{\Gamma(n+\frac{3}{2})}{\sqrt{\pi}} \frac{p^2/4}{(1+p^2/4)^{n+\frac{3}{2}}} \doteqdot x \cdot x^n J_n(2x) \qquad R(n) > -1$$

This changes by the application of $F_1$ into

$$2^{n+1} \frac{\Gamma(n+\frac{3}{2})}{\sqrt{\pi}} \frac{p^2}{(1+p^2)^{n+\frac{3}{2}}} \doteqdot x^{n+1} J_n(x) \ldots . R(n) > -1 \qquad (2\cdot2)$$

This result can also be obtained by applying to the operational representation obtained by Pol[6]

$$\frac{2^n \Gamma(n+\frac{1}{2})}{\sqrt{\pi}} \frac{p}{(1+p^2)^{n+\frac{1}{2}}} \doteqdot x^n J_n(x)$$

the theorem of operational calculus

$$p\left(-\frac{d}{dp}\right)\frac{f(p)}{p} \doteqdot x\, h(x) \text{ if } h(x) \doteqdot f(p).$$

(ii) Consider[7]

$$p^{-\frac{2m-n}{2}+1} J_n\left(-2\sqrt{\frac{1}{p}}\right) \doteqdot x^{\frac{1}{3}[2(m-1)-n]} J_{m-\frac{1}{3},\, n}(3\sqrt[3]{x})$$

and choose $m = \frac{1}{2}(2n+1)$ we get

$$g(x) = x^{\frac{n-1}{3}} \, J_{\frac{2n-1}{2}, n}(3\sqrt[3]{x})$$

$$\doteqdot \sqrt{p}\, p^{-\frac{n}{2}} J_n\left(-2\sqrt{\frac{1}{p}}\right)$$

$$= \sqrt{p}\, h\left(\frac{1}{p}\right).$$

Hence $h(x) = x^{\frac{n}{2}} J_n(-2\sqrt{x})$

$$= (-)^n x^{\frac{n}{2}} J_n(2\sqrt{x})$$

$$\doteqdot (-)^n p^{-n} e^{-\frac{1}{p}} = f(p)$$

where $n$ is an integer. Therefore from Theorem II we get

$$x^{\frac{1}{3}(2n+1)} \, J_{\frac{2n-1}{2}, n}(3x^{2/3}) \doteqdot \frac{(-)^n}{\sqrt{\pi}} \left(\frac{2}{p}\right)^{2n} e^{-\frac{4}{p^2}} \qquad (2\cdot3)$$

(iii) Consider

$$g(x) = e^{-x} x^m \, T_m^n(x) \doteqdot \frac{1}{p^{\mu-1}} \cdot \frac{(-)^n p^{n+\mu}}{\Gamma(n+1)(1+p)^{m+n+1}}.$$

$$= \frac{1}{p^{\mu-1}} h\left(\frac{1}{p}\right) \qquad R(m+n) > -1$$

from (1·7) with $F_9$.

Hence $h(x) = \dfrac{(-)^n}{\Gamma(1+n)} \dfrac{x^{m-\mu+1}}{(1+x)^{m+n+1}}.$

$$\doteqdot \frac{(-)^n \Gamma(m-\mu+2)}{\Gamma(1+n)} p^{\frac{1}{2}(n+\mu)} e^{\frac{1}{2}p} W_{-\frac{1}{2}(n-\mu+2m+2), -\frac{1}{2}(\mu+n-1)}(p)$$

$$= f(p) \qquad R(m-\mu+2) \geqslant 0.$$

by following the same method for obtaining the 'image' as was done in the case of (1·9) before. Therefore by Theorem III we get

$$\frac{(-)^n \Gamma(m-\mu+2)}{2\,\Gamma(n+1)} p^{\frac{1}{2}(n-1)} e^{\frac{1}{2}p} W_{-\frac{1}{2}(n-\mu+2m+2), -\frac{1}{2}(\mu+n-1)}(p)$$

$$= \int_0^\infty e^{-t} t^{m-\frac{1}{2}(\mu-1)} T_m^n(t) K_{\mu-1}(2\sqrt{pt})\, dt$$

Putting $\mu - 1 = 2l$ we have

$$\int_0^\infty e^{-t} t^{m-l} \mathrm{T}_m^n(t)\, \mathrm{K}_{2l}(2\sqrt{pt})\, dt$$

$$= \frac{(-)^n}{2\,\Gamma(n+1)}\, \Gamma(m-2l+1)\, p^{\frac{1}{2}(n-1)}\, e^{\frac{1}{2}p}\, \mathrm{W}_{-\frac{1}{2}(n+2m-2l+1),\,-\frac{1}{2}(2l+n)}(p) \qquad (2\cdot4)$$

$$p > 0 \quad \mathrm{R}(m+n) > -1 \text{ and } \mathrm{R}(m-2l+1) \geqslant 0.$$

(iv) Let[7] $\varphi(x) = x^{-\frac{1}{2}(m+n)}\, \mathrm{J}_{m,n}(3\sqrt[3]{x})$

$$\doteqdot (-)^n p^{-\frac{1}{2}(n-m)}\, \mathrm{J}_{n-m}\left(-\frac{2}{\sqrt{p}}\right) p^n$$

$$= p^n h\left(\frac{1}{p}\right)$$

Therefore $h(x) = (-)^n x^{\frac{n-m}{2}}\, \mathrm{J}_{n-m}(-2\sqrt{x})$

$$= (-)^m x^{\frac{n-m}{2}}\, \mathrm{J}_{n-m}(2\sqrt{x})$$

$$\doteqdot (-)^m p^{-(n-m)}\, e^{-\frac{1}{p}}$$

$$= f(p)$$

provided $n$ and $m$ are integers. Hence by Theorem III we get

$$(-)^m p^{m-n}\, e^{-\frac{1}{p}} = 2\, p^{-\frac{n}{2}+1} \int_0^\infty t^{\frac{1}{6}(2m)}\, \mathrm{J}_{m,n}(3\sqrt[3]{t})\, \mathrm{K}_{-n}(2\sqrt{pt})\, dt$$

Putting $\sqrt[3]{t} = x^2$, changing $p$ into $p^2$ and using $k_\nu(z) = k_{-\nu}(z)$ we get after simplification

$$\frac{(-)^m}{12}\, p^{2m-n-2}\, e^{-\frac{1}{p^2}} = \int_0^\infty x^{n-2m+5}\, \mathrm{J}_{m,n}(3x^2)\, k_n(2px^3)\, dx \qquad (2\cdot5)$$

$n$ and $m$ being integers. This gives a relation between the Bessel function of the third order and the Bessel function of the second kind.

(v) Now consider $\varphi(x) = x^{n-\frac{1}{2}} \cos(\sqrt{2x})$

$$\doteqdot (-)^n \sqrt{\pi}\, 2^{-n}\, \sqrt{p}\, e^{-\frac{1}{4}p}\, \mathrm{D}_{2n}\left(\frac{1}{\sqrt{p}}\right) \cdot \frac{1}{p^n}$$

$$= h\left(\frac{1}{p}\right) \cdot \frac{1}{p^n}.$$

an operational result obtained from Adamoff's integral[8] involving Weber's parabolic cylinder function. Therefore

$$h(x) = (-)^n \sqrt{\pi}\, 2^{-n}\, \frac{e^{-\frac{x}{4}}}{\sqrt{x}}\, D_{2n}(\sqrt{x})$$

But[9]

$$x^{-\frac{1}{2}} D_{2n}(2\sqrt{x}) \doteqdot \frac{\sqrt{\pi}\, 2n!\, p(1-p)^n}{2^n \cdot n!\, (1+p)^{n+\frac{1}{2}}}.$$

Hence by $F_1$ and $F_2$

$$\frac{e^{-\frac{x}{4}}}{\sqrt{x}}\, D_{2n}\sqrt{x} \doteqdot \frac{\sqrt{\pi}\, 2n!}{n!}\, \frac{(-)^n \sqrt{2}\, p^{n+1}}{(1+2p)^{n+\frac{1}{2}}}.$$

and therefore

$$h(x) \doteqdot \frac{\pi\, 2n!\, 2^{-n+\frac{1}{2}}\, p^{n+1}}{n!\, (1+2p)^{n+\frac{1}{2}}} = f(p)$$

Hence from Theorem III we get

$$\int_0^\infty z^{\frac{n-1}{2}} \cos\sqrt{\frac{2z}{p}}\, K_n(2\sqrt{z})\, dz = \frac{\pi\, 2n!}{n!\, 2^{n+\frac{1}{2}}} \left(2 + \frac{1}{p}\right)^{-n-\frac{1}{2}} \qquad (2\cdot6)$$

an integral more general than the one already given. [Watson, B. F., p. 388 (10)].

Similarly, if we consider the operational relations

$$\sin\sqrt{2x} \doteqdot (-)^n 2^{-n-\frac{1}{2}} \sqrt{\pi}\, e^{-\frac{1}{4p}}\, \frac{1}{p^n}\, D_{2n+1}\left(\frac{1}{\sqrt{p}}\right).$$

and[9]

$$D_{2n+1}(\sqrt{x}) \doteqdot \frac{\sqrt{\pi}\,(2n+1)!}{2^n\, n!}\, \frac{4p(1-4p)^n}{(1+4p)^{n+\frac{3}{2}}}$$

and proceed on lines similar to the above we will get the integral

$$\int_0^\infty z^{\frac{n}{2}} \sin\sqrt{\frac{2z}{p}}\, K_n(2\sqrt{z})\, dz = \frac{\pi(2n+1)!}{2^{n+1}\, n!}\, \frac{p^{n+1}}{(1+2p)^{n+\frac{3}{2}}} \qquad (2\cdot7)$$

(vi) Take

$$f(p) = \frac{p}{1+p^2} \doteqdot \sin x = h(x)$$

Therefore

$$h\left(\frac{1}{p}\right) = \sin\frac{1}{p} \doteqdot \mathrm{bei}(2\sqrt{x}) = g(x)$$

Hence

$$\frac{1}{1+p^2} = 2\int_0^\infty \mathrm{bei}(2\sqrt{t})\, K_0(2\sqrt{pt})\, dt \qquad (2\cdot8)$$

Similarly if we start with $\frac{p^2}{1+p^2} \doteqdot \cos x$ we get

$$\frac{p}{1+p^2} = 2\int_0^\infty \mathrm{ber}\,(2\sqrt{t})\,\mathrm{K}_0\,(2\sqrt{pt})\,dt \qquad (2\cdot9)$$

(vii) As the last example consider

$$f(p) = \frac{1}{p^n} \doteqdot \frac{x^n}{\Gamma(1+n)} = h(x)$$

Hence

$$\frac{1}{p^s}\,h\left(\frac{1}{p}\right) = \frac{1}{\Gamma(1+n)\,p^{s+n}}$$

$$\doteqdot \frac{x^{s+n}}{\Gamma(1+n)\,\Gamma(1+n+s)} = g(x)$$

Therefore by applying the theorem and the substitution $pt = \frac{x^2}{4}$ we get

$$2^{2n+s}\,\Gamma(n+1)\,\Gamma(n+s+1) = \int_0^\infty x^{2n+s+1}\,\mathrm{K}_s(x)\,dx \qquad (2\cdot10)$$

a result given in Watson's *B.F.*, p. 388.

III. We will conclude this paper by proving the following theorem.

THEOREM IV.—If $f(p) \doteqdot h(x)$: $h(p)p^{1-n} \doteqdot g(x)$ and $g(p)\,p^{1-m} \doteqdot j(x)$ then

$$f(q) = \Gamma(1+n)\,\Gamma(1+m)\,p^{m-n} \times$$

$$\times \int_0^\infty e^{\frac{\xi}{2}}\,\xi^{\frac{1}{2}(n-m-1)}\,\mathrm{W}_{-\frac{1}{2}(n+m+1),\,\frac{1}{2}(n-m)}(\xi)\;j\left(\frac{\xi}{p}\right)d\xi$$

$$\mathrm{R}(m+1) \geqslant 0 \text{ and } \mathrm{R}(n+1) \geqslant 0.$$

The proof of this theorem can be easily deduced. For this we have to reverse the order of integration twice. After the first inversion of the order of integration we use (1·2) to evaluate the integral occurring in the result. Then we proceed with the second inversion and use (1·8) and the substitution $px = \xi$. We then get the theorem after little simplification. The process of inversion is justifiable if $\mathrm{R}(m) > -1$, $j(x)$ is bounded and integrable in $x > 0$ and $\int_0^a |j(x)|\,dx$ is bounded in $x > 0$, and the last integral involving Whittaker's function and $j(x)$ is convergent. We will now consider two examples on this theorem.

(i) Let [10] $j(x) = e^{-\frac{x}{2}} N_{k,l}(x)$

$$\doteqdot \frac{p^{k-l+\frac{1}{2}}}{(1+p)^{k+l+\frac{1}{2}}}$$

$$= g(p) \cdot p^{l-m}$$

Hence $$g(x) = \frac{x^{k+m-l-\frac{1}{2}}}{(1+x)^{k+l+\frac{1}{2}}}$$

$$\doteqdot \Gamma(k+m-l+\tfrac{1}{2})\, e^{\frac{1}{2}p}\, p^{l-\frac{m}{2}+\frac{1}{2}} \times$$

$$W_{-k-\frac{m}{2},\ -l+\frac{m}{2}}(p) \qquad R(k-l+m+1) \geqslant 0$$

by using a process similar to one used in getting the operational representation in (1·9). Denoting the operational representation of $g(x)$ by $h(p)\, p^{1-n}$, we have

$$h(x) = \Gamma(k+m-l+\tfrac{1}{2})\, e^{\frac{1}{2}x}\, x^{l+n-\frac{m+1}{2}} W_{-k-\frac{m}{2},\ -l+\frac{m}{2}}(x)$$

$$\doteqdot \frac{\Gamma(k+m-l+\frac{1}{2})\ \Gamma(-k-l+\frac{1}{2})\ \Gamma(l-k-m+\frac{1}{2})}{\Gamma(-k-l-n+\frac{1}{2})}$$

$$\times p(1-p)^{-k-l-n-\frac{1}{2}}\ {}_2F_1\left[\begin{matrix}-k-l+\frac{1}{2},\ -k+l-m+\frac{1}{2}, \\ -k-l-n+\frac{1}{2};\ (1-p)\end{matrix}\right].$$

$$= f(p)$$

using the operational representation of Whittaker's function as given by Dhar[11]

$$x^{l-1}\, e^{-\frac{1}{2}x}\, W_{k,m}(x) \doteqdot \frac{\Gamma(m+k+\frac{1}{2})\ \Gamma(-m+k+\frac{1}{2})}{\Gamma(k-l+1)}$$

$$\times p(-p)^{k-l}\ {}_2F_1\left[\begin{matrix}m+k+\frac{1}{2}, k-m+\frac{1}{2} \\ k-l+1\ ;\ -p\end{matrix}\right].$$

with $F_2$. Hence we have by the application of Theorem IV the integral

$$\int_0^\infty e^{\frac{x}{2}\left(t-\frac{1}{p}\right)}\, x^{\frac{1}{2}(n-m-1)}\, W_{-\frac{1}{2}(n+m+1),\ \frac{1}{2}(n-m)}(x)\, N_{k,l}\left(\frac{x}{p}\right) dx$$

$$= \frac{\Gamma(k+m-l+\frac{1}{2})\ \Gamma(-k-l+\frac{1}{2})\ \Gamma(l-k-m+\frac{1}{2})}{\Gamma(-k-l-n+\frac{1}{2})\ \Gamma(1+n)\ \Gamma(1+m)}\, p^{n-m+1}(1-p)^{-k-l-n-\frac{1}{2}}$$

$$\times {}_2F_1[-k-l+\tfrac{1}{2},\ -k+l-m+\tfrac{1}{2},\ -k-l-n+\tfrac{1}{2};(1-p)] \quad (3\cdot1)$$

$$R(m+1) > 0,\ R(n+1) > 0 \text{ and } R(k-l+m+1) \geqslant 0$$

(ii) Let $j(x) = x^{\frac{l}{2}} J_l(2\sqrt{x})$

$$\doteqdot p^{-l} e^{-\frac{1}{p}} \qquad R(l) > -1$$

$$= p^{m-l-1} e^{-\frac{1}{p}} p^{1-m}$$

$$= g(p) \cdot p^{1-m}$$

Hence $g(x) = x^{m-l-1} e^{-\frac{1}{x}}$

$$\doteqdot 2p^{1-\frac{m-l}{2}} K_{m-l}(2\sqrt{p})$$

$$= 2p^{n-\frac{m-l}{2}} K_{m-l}(2\sqrt{p})\, p^{1-n}$$

$$= h(p) \cdot p^{1-n}$$

from (1·5), where $K_s$ denotes the Bessel function of the second kind. Again we have from the integral[12]

$$\int_0^\infty e^{-\xi^2 u^2} k_{2m}(2\xi u)\, u^{-2k}\, du = \frac{\Gamma(\frac{1}{2}+m-k)\,\Gamma(\frac{1}{2}-m-k)}{4\xi}\, e^{\frac{1}{2}\xi^2} W_{k,m}(\xi^2)$$

$$R(\tfrac{1}{2} \pm m - k) > 0$$

by using the substitutions $\xi u = \sqrt{x}$ and $\xi = \frac{1}{\sqrt{p}}$, $p$ positive and the definition of the operational representation,

$$2x^{-k-\frac{1}{2}} k_{2m}(2\sqrt{x}) \doteqdot \Gamma(\tfrac{1}{2}+m-k)\,\Gamma(\tfrac{1}{2}-m-k)\, e^{\frac{1}{2p}} p^{k+1} W_{k,m}\left(\frac{1}{p}\right) \quad (3\cdot2)$$

Hence

$$h(x) = 2x^{n-\frac{1}{2}(m-l)} K_{m-l}(2\sqrt{x})$$

$$\doteqdot \Gamma(n+1)\,\Gamma(n-m+l+1)\, p^{-n+\frac{1}{2}(m-l+1)}\, e^{\frac{1}{2p}} \times$$

$$\times W_{-n+\frac{1}{2}(m-l-1),\,\frac{1}{2}(m-l)}\left(\frac{1}{p}\right)$$

$$= f(p) \qquad R(n+1) > 0 \text{ and } R(n-m+l+1) > 0$$

Therefore from Theorem IV we have

$$\int_0^\infty e^{-\frac{x}{2}} x^{\frac{1}{2}(l+n-m-1)} W_{-\frac{1}{2}(n+m+1),\,\frac{1}{2}(n-m)}(x)\, J_l\left(2\sqrt{\frac{x}{p}}\right) dx$$

$$= \frac{\Gamma(n-m+l+1)}{\Gamma(1+m)}\, p^{\frac{1}{2}(l-m)}\, e^{\frac{1}{2p}} W_{-n+\frac{1}{2}(m-l-1),\,\frac{1}{2}(m-l)}\left(\frac{1}{p}\right) \quad (3\cdot3)$$

provided

$$R(m+1) > 0,\ R(n+1) > 0 \text{ and } R(n-m+l+1) > 0$$

The substitutions

$$l = \nu,\ p = \frac{1}{s},\ n = -(m' + k' + \tfrac{1}{2}),\ m = (m' - k' - \tfrac{1}{2})$$

change this result into the Hankel transform of the Whittaker's function obtained by Erdelyi.[13]

If $m = n = 1$. Theorem IV reduces to a simpler form as:

THEOREM V.–If $f(p) \doteqdot h(x)$; $h(p) \doteqdot g(x)$ and $g(p) \doteqdot j(x)$ then

$$f(p) = \int_0^\infty e^{\frac{x}{2}}\, x^{-\frac{1}{2}}\, W_{-\frac{3}{2},\,0}(x)\, j\left(\frac{x}{p}\right) dx$$

As an application of this theorem consider the series of operational representations;

$$f(p) = \log p \doteqdot -\gamma - \log(x) = h(x)$$

$$h(p) = -\gamma - \log(p) \doteqdot \log(x) = g(x)$$

and

$$g(p) = \log p \doteqdot -\gamma - \log(x) = j(x)$$

Hence

$$-\log p = \int_0^\infty e^{\frac{x}{2}}\, x^{-\frac{1}{2}}\, W_{-\frac{3}{2},\,0}(x) \left[\gamma + \log\frac{x}{p}\right] dx \qquad (3\cdot4)$$

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# MAGNETIC SUSCEPTIBILITIES OF CALCIUM AND STRONTIUM IONS

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Prasad, Dharmatti and Kanekar[1] have recently measured the susceptibilities of a number of barium salts of inorganic and organic acids, and using the available values of the anions they have determined the ionic susceptibility of barium. They found that the values calculated from the salts of inorganic acids agree well with those theoretically calculated according to Slater's[2] and Angus's[3] methods, and that the values deduced from the susceptibilities of salts of organic acids are higher than these values. This paper gives the results of the measurements of susceptibilities of calcium and strontium salts of several inorganic and organic acids. The data obtained have been utilised to calculate the susceptibilities of calcium and strontium ions, using all the possible available values of anions and assuming the applicability of the additivity law. The results obtained have been statistically examined and the significance of the observed differences in their values deduced by using values for anions from different sources has been determined. The ionic susceptibilities evaluated from the data on inorganic salts have been compared with those deduced from the data on salts of organic acids with a view to examine the findings of the previous workers. Ionic radii of calcium and strontium ions have also been estimated from their ionic susceptibilities and the values thus obtained have been compared with those obtained on the basis of other considerations.

The susceptibilities of many of the compounds studied in this investigation do not seem to have been measured so far; thus the data given in this paper consists of (*i*) the unknown values of the susceptibilities of many known compounds and (*ii*) the revised values of the susceptibilities of compounds, investigated previously by other workers. A large number of salts of calcium and strontium has been used in this investigation since the accuracy of the deduced values of the ionic susceptibilities is higher, greater is the number of salts whose susceptibilities are used for averaging, wherever such a procedure is valid.

The values of the susceptibilities of some salts have also been computed from Bhatnagar's theory of electronic isomers[4] and compared with the experimental values.

Some of the previous workers have deduced the susceptibilities of salts from measurements made on their solutions in water but in thisi nvestigation all the measurements have been made on solid compounds mainly because the theoretical position regarding the state of ionisation in solution and the effect of ions on the molecules of the solvent is not satisfactorily settled.[5]

*Experimental*

The measurement of the susceptibilities was made by a magnetic balance of Gouy type in which several refinements were introduced. Some of the important features are described in this paper and complete details are being published elsewhere.

The electromagnet employed so far in our previous investigations used to get heated, and the errors introduced thereby were avoided by a number of adjustments. Consequently a magnet was designed which with a low current (0·7 amps.) at 230 volts could give fairly high fields necessary for susceptibility measurements. The windings (Helico solenoidal) of the magnet were made in eight sections and the total resistance of the windings was 270 ohms. at 30°. The yoke of the magnet was made of the best quality dynamo steel of low hysteresis. The semi-angle of the pole pieces was 27° 22′ and the area of the pole pieces was 1 square inch. It was observed that the magnet showed no rise of temperature for half an hour's continuous run when kept open in a room, but in the casing of the magnetic balance the temperature rose by 0·1°. The field between a pole gap of 1 cm. was found to be 7,500 gauss.

In order to maintain constant current through the electromagnet the voltage fluctuations were guarded by introducing two series rheostats of 100 ohms rated at 1 amp. each, as ballast resistances.

The sensitivity of the balance was adjusted to 4 divisions per mg. The upthrust of the tube carrying the substance whose susceptibility was required was measured by means of the shift of a 5 mg. rider. This gave an accuracy of 0·0001 gm. in weight measurements.

The tube used for containing substances was machine drawn. It was made of 1/16″ pyrex glass, was 3·5 cm. long and 0·6 cm. wide (inside diameters) and its capacity was about 3·0 c.c. This tube was suspended by an arrangement which satisfies practically all the theoretical conditions. The general disposition of the several parts of the apparatus was such that its working was quite easy and convenient.

The substance to be investigated was first crushed into a fine powder and dried, and then introduced into the tube through a thistle-shaped funnel

by the aid of a rod, upto a certain mark made on the tube. The substance was pressed home by means of a ram-rod so that the theoretical condition of closest and uniform packing is reached as approximately as possible. The tube was closed by a ground-glass stopper soon after filling to prevent any contamination of the substance with moisture.

After each experiment the substance was taken out of the tube by means of a small glass spade and the tube was cleaned with tap water, dilute chromic acid, distilled water, and absolute alcohol and then dried before use.

### *Method of Working*

Every compound studied was experimented upon in two different ways: (*i*) two readings were taken for different packings in a given tube, each of these readings being the mean of four observations and (*ii*) the same procedure was repeated in another tube. The shift values employed for the calculation of molar susceptibilities were thus the mean of sixteen readings. The result was the mean of four susceptibility values. This procedure was good enough to smooth out errors due to heterogeneity or looseness of packing. By way of check on the procedure, empty tube readings were taken in between every set of observations and the balance was periodically calibrated with Kahlbaum's or Merck's extra pure KCl, Te and Se.

The magnetic susceptibility was calculated from the relation

$$\chi = \frac{1}{m}\left[(\chi_1 m_1 - \chi_a m_{a1})\frac{d_2 - d_a}{d_1 - d_a} + \chi_a m_a\right]$$

where the terms involved have the usual meaning.

In any set of experiments the shift values of the rider for a filled tube were found to be nearly the same for all observations. This shows that the packing was of nearly the same closeness throughout, the volumes to which the tubes were filled were nearly the same, and there were no fluctuations due to heating. The maximum variations in the shift values were of the order of about 1 per cent. for several substances used in this investigation. The reproducibility of the results was therefore high; the average error in the susceptibility values was nearly 5 per cent.

### *Substances Used*

The compounds studied are the calcium and strontium salts of inorganic and organic acids. Some of these were either Kahlbaum's or Merck's products of extra pure quality [indicated as (1) and (2), respectively in Tables I and II] and others were either purified by recrystallisation or prepared in the laboratory and were analysed for their purity before use.

### *Results*

The results obtained are given in Tables I and II in which the quality of the substances used is given in column 1, and N, the total number of electrons in the molecules of the anhydrous compound in column 2. In order to compare the observed values (column 3) with the experimental values obtained by previous workers (column 4) and with those computed by summing the experimental values of cations and anions derived by the same worker (column 5) the observed molar susceptibilities for the anhydrous salts were obtained from the values of the hydrated susbtances by subtracting the accepted values (12·96), the molar susceptibility of water, for every molecule of water of hydration. The same procedure has been followed by Kido and other workers. This, however, takes away some of the rigour of the investigation as it tacitly assumes an additivity for the susceptibility of the water of crystallisation, but the effect of hydration in compounds containing water of crystallisation is not so simple, for the surrounding water molecules of co-ordination become saturated and distorted (*cf.* Sack[6]). Raichaudhari[7] and others have attempted to correlate the change of susceptibility due to the presence of water molecules of co-ordination with the corresponding heats of hydration, but an exact quantitative description of the phenomenon is not known. In the absence of such a relation, the process of subtracting seems justifiable and may be adopted. The values of specific susceptibilities ($\chi_a$) and molar susceptibilities ($\chi_m$) of salts and molar susceptibilities of anhydrous salts ($\chi_{ma}$) are given in the third column of the tables.

All susceptibility values given in this paper are expressed in units of $(-1 \times 10^{-6})$ c.g.s. units.

### *Discussion of Results*

It will be seen from the above tables that the values of the susceptibilities of many substances obtained by the authors are in fair agreement with those found by some of the previous workers (*cf.* columns 3 and 4 of Tables I and II) within the limits of error found in this investigation. The observed differences in the other cases may either be due to (*i*) impurities in the substances used, or (*ii*) different physical state of the substances employed, or (*iii*) the data being obtained from measurements on solutions in cases wherein the solution law is not rigorously applicable.

Angus[3] and Farquharson[8] have developed a method for the calculation of the susceptibilities of ions containing more than one dissimilar atom by summing up the susceptibilities of the constitutent atoms in the desired ionic state. Thus according to this method the susceptibility of the sulphate ion is

TABLE I

| Compounds | N | Authors' values | $\chi_{ma}$ Other workers | | $\chi_{ma}$ Computed experimentally | $\chi_{ma}$ Computed theoretically |
|---|---|---|---|---|---|---|
| | | | *(a) Calcium salts of inorganic acids* | | | |
| $CaBr_2\,3H_2O$ (1) .. .. | 90 | $\chi_a$ = 0·453<br>$\chi_m$ =115·1<br>$\chi_{ma}$= 76·22 | Luther | 54·55 | 73·2 (Pascal)<br>73·48 (Pascal)<br>78·4 (Hoccart)<br>80·6 (Ikenmeyer)<br>79·6 (Weiss)<br>72·0 (Brindley)<br>75·9 (Kido) | $Ca^{+2}+2\,Br^{-1}$<br>121·3<br>91·58<br>83·72 |
| $CaCO_3$ (2) .. .. | 50 | $\chi_a$ = 0·37<br>$\chi_m$ = 37·37<br>$\chi_{ma}$= 37·37 | Pascal<br>Dhawan<br>Kido<br>Raman & Krishnan—<br>Aragonite<br>Calcite | 38·2<br>14·01<br>35·5<br><br>40·08<br>37·8 | 34·4 (Pascal)<br>34·6 (Kido) | $Ca^{+2}+C^{+4}+3\,0^{-2}$<br>51·25<br>50·98<br>44·32 |
| $CaCl_2$ (anhydrous) (1) .. | 54 | $\chi_a$ = 0·480<br>$\chi_m$ = 53·4<br>$\chi_{ma}$= 53·4 | Quincke (aq. sol.)<br>Königsberger (aq. sol.)<br>Meyer (solid)<br>Ikenmeyer (aq. sol.)<br>Hoccart (aq. sol.)<br>(solid) | 41·41<br>43·43<br>49·49<br>51·7<br>55·6<br>54·45 | 51·4 (Pascal)<br>56·8 (Hoccart)<br>51·8 (Ikenmeyer)<br>57·6 (Weiss)<br>58·0 (Brindley)<br>50·7 (Kido) | $Ca^{+2}+2\,Cl^{-1}$<br>71·30<br>62·96<br>56·14 |
| $CaCrO_4 \cdot 2\,H_2O$<br>Ca found = 20·17%<br>Ca theory = 20·9% | 76 | $\chi_a$ = 0·0468<br>$\chi_m$ = 9·030<br>$\chi_{ma}$= 16·89 | .. | | .. | $Ca^{+2}+Cr^{+6}+4\,0^{-2}$<br>70·30<br>69·48<br>60·57 |
| $CaF_2$ (1) (2) .. .. | 38 | $\chi_a$ = 0·339<br>$\chi_m$ = 26·5<br>$\chi_{ma}$= 26·5 | Meyer<br>Voigt & Kinoshita<br>Ishiwara<br>Pascal | 23·4<br>15·6<br>22·25<br>28·1 | 23·1 (Pascal)<br>24·8 (Pascal)<br>23·2 (Pascal)<br>38·8 (Ikenmeyer)<br>34·0 (Brindley)<br>30·9 (Kido) | $Ca^{+2}+2\,F^{-1}$<br>29·5<br>27·98<br>24·92 |
| $Ca(OH)_2$ (2) .. .. | 38 | $\chi_a$ = 0·300<br>$\chi_m$ = 22·23<br>$\chi_{ma}$= 22·23 | Meyer<br>Kido | 28·9<br>21·3 | 18·74 (Pascal) | $Ca^{+2}+2\,(OH)^{-1}$<br>38·5<br>37·68<br>32·92 |
| $Ca(NO_3)_2$ (1) .. .. | 82 | $\chi_a$ = 0·287<br>$\chi_m$ = 47·1 | Kido | 46·0 | 39·6 (Pascal)<br>46·7 (Kido) | $Ca^{+2}+6O^{-2}+2\,N^{+5}$<br>89·12 |

| | | | | | | |
|---|---|---|---|---|---|---|
| $Ca(NO_3)_2$ (1) .. .. | 82 | $\chi_a = 0{\cdot}287$<br>$\chi_m = 47{\cdot}1$<br>$\chi_{ma} = 47{\cdot}1$ | Kido | 46·0 | 39·6 (Pascal)<br>46·7 (Kido) | $Ca^{+2}+6O^{-2}+2N^{+5}$<br>89·12<br>90·46<br>78·14 |
| CaO (2) .. .. .. | 28 | $\chi_a = 0{\cdot}270$<br>$\chi_m = 15{\cdot}14$<br>$\chi_{ma} = 15{\cdot}14$ | Meyer<br>Dhawan | 15·13<br>15·74 | 15·81 (Pascal) | $Ca^{+2}+O^{-2}$<br>25·9<br>24·53<br>21·67 |
| $CaSO_4 \cdot 2H_2O$<br>Ca found = 23·3%<br>Ca theory = 23·35% | 68 | $\chi_a = 0{\cdot}433$<br>$\chi_m = 74{\cdot}6$<br>$\chi_{ma} = 48{\cdot}68$ | Meyer<br>Pascal<br>Dhawan<br>Kido | 51·8<br>49·6<br>51·73<br>46·8 | 44·8 (Pascal)<br>45·5 (Kido) | $Ca^{+2}+S^{+6}+4O^{-2}$<br>65·1<br>65·39<br>56·73 |

### (*b*) *Calcium salts of organic acids*

| | | | | | | |
|---|---|---|---|---|---|---|
| $(CH_3COO)_2Ca$<br>Ca found = 25·31%<br>Ca theory = 25·4% | 82 | $\chi_a = 0{\cdot}433$<br>$\chi_m = 68{\cdot}4$<br>$\chi_{ma} = 68{\cdot}4$ | Kido | 70·5 | 69·0 (Pascal)<br>70·5 (Kido)<br>69·3 (Kido) | $Ca^{+2}+2(CH_3COO)^{-1}$<br>70·82<br>68·9<br>67·94 |
| $(HCOO)_2Ca$<br>Ca found = 30·78%<br>Ca theory = 30·8% | 66 | $\chi_a = 0{\cdot}348$<br>$\chi_m = 45{\cdot}3$<br>$\chi_{ma} = 45{\cdot}3$ | Rao & Sriraman<br>Rao & Sriraman (aq. sol.) | 39·5<br>39·9 | 45·0 (Pascal)<br>46·9 (Kido) | $Ca^{+2}+2(HCOO)^{-1}$<br>47·1<br>45·18<br>44·22 |
| $(C_3H_5O_3)_2Ca \cdot 5H_2O$ (2) | 114 | $\chi_a = 0{\cdot}609$<br>$\chi_m = 187{\cdot}5$<br>$\chi_{ma} = 122{\cdot}7$ | .. | | .. | $Ca^{+2}+2(C_3H_5O_3)^{-1}$<br>103·76<br>101·84<br>100·88 |
| $CaC_2O_4$<br>Ca found = 31·29%<br>Ca theory = 31·35% | 64 | $\chi_a = 0{\cdot}346$<br>$\chi_m = 44{\cdot}3$<br>$\chi_{ma} = 44{\cdot}3$ | .. | | 39·16 (Pascal) | $Ca^{+2}+(C_2O_4)^{-2}$<br>41·24<br>38·38<br>39·32 |
| $(C_6H_4OHCOO)_2Ca \cdot 3H_2O$<br>Ca found = 9·98%<br>Ca theory = 10·9% | 162 | $\chi_a = 0{\cdot}546$<br>$\chi_m = 200{\cdot}9$<br>$\chi_{ma} = 162{\cdot}02$ | .. | | 153·08 (Pascal | $Ca^{+2}+2(C_6H_4OHCOO)^{-1}$<br>154·64<br>151·76<br>152·76 |
| $CaC_4H_4O_6 \cdot 4H_2O$<br>Ca found = 15·38%<br>Ca theory = 15·40% | 96 | $\chi_a = 0{\cdot}464$<br>$\chi_m = 120{\cdot}2$<br>$\chi_{ma} = 68{\cdot}36$ | .. | | 65·94 (Pascal) | $Ca^{+2}+(C_4H_4O_6)^{-2}$<br>74·18<br>72·26<br>71·30 |

TABLE II

| Compounds | N | Authors' values | $\chi_{ma}$ Other workers | | $\chi_{ma}$ Computed experimentally | $\chi_{ma}$ Computed theoretically |
|---|---|---|---|---|---|---|
| *(a) Strontium salts of inorganic acids* | | | | | | |
| $SrBr_2$ (2) .. .. | 108 | $\chi_a = 0{\cdot}352$<br>$\chi_m = 86{\cdot}63$<br>$\chi_{ma} = 86{\cdot}3$ | Meyer<br>Meyer<br>Meyer<br>Ikenmeyer (aq. sol.) | 76·6<br>96·25<br>76·6<br>87·3 | 81·6 (Pascal)<br>81·88 (Pascal)<br>86·7 (Hoccart)<br>95·0 (Ikenmeyer)<br>85·0 (Kido) | $Sr^{+2}+2\,Br^{-1}$<br>136·00<br>101·70<br>93·49 |
| $SrCO_3$ (2) .. .. | 68 | $\chi_a = 0{\cdot}322$<br>$\chi_m = 47{\cdot}23$<br>$\chi_{ma} = 47{\cdot}23$ | Pascal<br>Dhawan<br>Kido | 46·6<br>25·25<br>44·2 | 42·8 (Pascal)<br>43·7 (Kido) | $Sr^{+2}+(CO_3)^{-2}$<br>65·95<br>61·13<br>54·09 |
| $SrCl_2$ (2) .. .. | 72 | $\chi_a = 0{\cdot}402$<br>$\chi_m = 63{\cdot}6$<br>$\chi_{ma} = 63{\cdot}6$ | Königsberger (aq. sol.)<br>Meyer (solid)<br>Meyer (solid)<br>Ikenmeyer (aq. sol.)<br>Ikenmeyer (aq. sol.)<br>Kido | 63·4<br>88·6<br>69·6<br>53·5<br>61·6<br>61·3 | 60·8 (Pascal)<br>65·1 (Hoccart)<br>66·2 (Ikenmeyer)<br>59·8 (Kido) | $Sr^{+2}+2\,Cl^{-1}$<br>86·00<br>76·11<br>65·91 |
| $SrCrO_4$<br>Sr found = 43·1%<br>Sr theory = 43·13% | 94 | $\chi_a = -0{\cdot}0252$<br>$\chi_m = -5{\cdot}09$<br>$\chi_{ma} = -5{\cdot}09$ | .. | | .. | $Sr^{+2}+Cr^{+6}+4\,0^{-2}$<br>85·0<br>79·63<br>70·34 |
| $Sr(OH)_2$ (2) .. .. | 56 | $\chi_a = 0{\cdot}417$<br>$\chi_m = 40{\cdot}4$<br>$\chi_{ma} = 40{\cdot}4$ | Kido | 32·1 | 35·68 (Pascal) | $Sr^{+2}+2\,(OH)^{-1}$<br>53·2<br>47·83<br>42·62 |
| $SrSO_4$ (2) .. .. | 96 | $\chi_a = 0{\cdot}328$<br>$\chi_m = 60{\cdot}3$<br>$\chi_{ma} = 60{\cdot}3$ | Pascal (solid)<br>Pascal (mean value from orthorhombic crystals)<br>Kido (solid) | 57·9<br>58·8<br>52·4 | 54·2 (Pascal)<br>54·6 (Kido) | $Sr^{+2}+S^{+6}+4\,0^{-2}$<br>79·8<br>75·54<br>66·5 |

| | | | | | | |
|---|---|---|---|---|---|---|
| $Sr(NO_3)_2 \cdot 4\,H_2O$ (1) .. | 100 | $\chi_a = 0{\cdot}359$ | Kido | 54·7 | 49·0 (Pascal) | $Sr^{+2}+2\,N^{+5}+6\,0^{-2}$ |

| | | | | | | |
|---|---|---|---|---|---|---|
| $Sr(NO_3)_2 \cdot 4H_2O$ (1) .. | 100 | $\chi_a = 0{\cdot}359$<br>$\chi_m = 101{\cdot}7$<br>$\chi_{ma} = 57{\cdot}86$ | Kido | 54·7 | 49·0 (Pascal)<br>55·8 (Kido) | $Sr^{+2}+2N^{+5}+6O^{-2}$<br>103·82<br>100·65<br>87·91 |
| SrO (2) .. .. | 46 | $\chi_a = 0{\cdot}34$<br>$\chi_m = 35{\cdot}22$<br>$\chi_{ma} = 35{\cdot}22$ | Pascal<br>Luther | 61·88<br>25·04 | 25·210 (Pascal) | $Sr^{+2}+O^{-2}$<br>40·60<br>34·68<br>31·44 |

### (*b*) *Strontium salts of organic acids*

| | | | | | | |
|---|---|---|---|---|---|---|
| $(CH_3COO)_2Sr \cdot \frac{1}{2} H_2O$<br>Sr found = 40·0%<br>Sr theory = 40·08% | 100 | $\chi_a = 0{\cdot}318$<br>$\chi_m = 87{\cdot}7$<br>$\chi_{ma} = 81{\cdot}22$ | Kido | 79·1 | 78·4 (Pascal)<br>79·6 (Kido)<br>78·4 (Kido) | $Sr^{+2}+2(CH_3COO)^{-1}$<br>85·52<br>79·05<br>77·71 |
| $SrC_2O_4 \cdot H_2O$<br>Sr found = 45·1%<br>Sr theory = 45·3% | 82 | $\chi_a = 0{\cdot}349$<br>$\chi_m = 67{\cdot}6$<br>$\chi_{ma} = 54{\cdot}64$ | .. | | 48·54 (Pascal) | $Sr^{+2}+(C_2O_4)^{-2}$<br>55·94<br>49·47<br>48·13 |
| $(HCOO)_2Sr$<br>Sr found = 49·0%<br>Sr theory = 49·3% | 82 | $\chi_a = 0{\cdot}339$<br>$\chi_m = 60{\cdot}3$<br>$\chi_{ma} = 60{\cdot}3$ | .. | | 54·4 (Pascal)<br>56·0 (Kido) | $Sr^{+2}+2(HCOO)^{-1}$<br>61·8<br>55·33<br>53·99 |
| $(C_6H_4OHCOO)_2Sr \cdot 2H_2O$<br>Sr found = 22·0%<br>Sr theory = 22·18% | 180 | $\chi_a = 0{\cdot}508$<br>$\chi_m = 202{\cdot}2$<br>$\chi_{ma} = 176{\cdot}28$ | .. | | 163·48 (Pascal) | $Sr^{+2}+2(C_6H_4OHCOO)^{-1}$<br>169·34<br>162·82<br>161·54 |
| $SrC_4H_4O_6 \cdot 4H_2O$<br>Sr found = 28·1%<br>Sr theory = 28·5% | .. | $\chi_a = 0{\cdot}457$<br>$\chi_m = 140{\cdot}5$<br>$\chi_{ma} = 88{\cdot}66$ | .. | | 75·34 (Pascal) | $Sr^{+2}+(C_4H_4O_6)^{-2}$<br>88·88<br>82·41<br>81·07 |

given by the sum of susceptibilities of $S^{+6}$ and $4O^{-2}$ ions. This value of the sulphate ion when added to the susceptibility of a cation would give the susceptibility of the particular sulphate. Angus found that the values of susceptibilities of several beryllium salts calculated according to the above-mentioned scheme by using the values of ionic susceptibilities calculated according to his method agree fairly well with those found experimentally. However, Farquharson found wide divergences between the theoretical and experimental values, which he expected and explained as due to addition reactions and the relative increase in the weak paramagnetism which is independent of temperature. He utilised these differences to calculate the relative polarities of some of the bonds. The susceptibility values of the salts used in this investigation have been calculated according to the above scheme, employing the values for various ions calculated by Pauling, Slater and Angus. These values are given in column 6 of Tables I and II under the heading $\chi_{ma}$ (theor.) in the order P, S and A. It will be seen that nearly in all cases the calculated values do not agree with the observed ones for the anhydrous salts. These observations are similar to those made by Farquharson.

Pauling has computed the values of susceptibilities for some anions regarding them as mono-nuclear systems. The sum of these values and the values of cations also calculated by him in required molecular proportions would give the susceptibility of a salt. These values differ considerably from the observed values and thus point to the uncertainty in the method of calculation adopted by Pauling.

Interesting results are obtained when the values of $\chi_{ma}$ for the same salts of calcium, strontium and barium are plotted against N. The values of $\chi_{ma}$ for barium salts are those obtained by Prasad, Dharmatti and Kanekar.[1]

The curves drawn are shown in Fig. 1. Curves of this type have been drawn by Ikenmeyer,[9] Kido,[10] Trew,[11] and Prasad, Dharmatti and Kanekar[1]; the first three found that they are linear, while the last named observed that the various points on the graph do not lie on a straight line. Trew also noticed some deviations which are explained as " specific effects due to the crystalline forms of the compounds investigated ", but it appears to the authors that the observed divergences are due to different susceptibility contributions of the different anions. It will be seen that the various curves in Fig. 1 are not linear and hence these results are not in accordance with the observations of Ikenmeyer, Kido and Trew, while they support the findings of Prasad and co-workers.

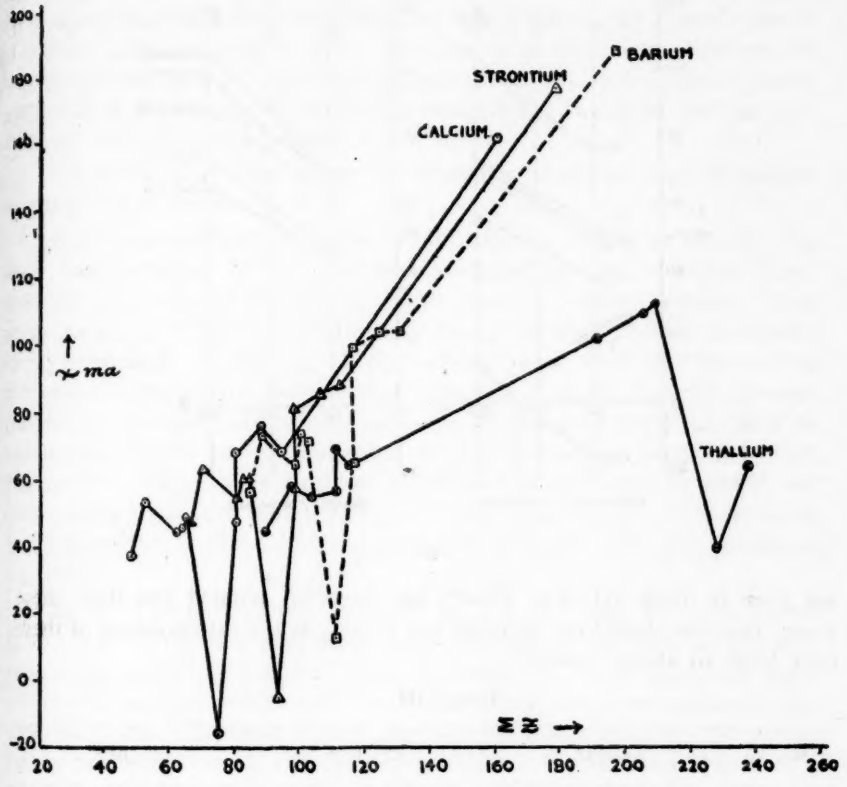


FIG. 1

Further it will be noticed that in each individual curve there is a pattern which is similar for the salts of the three elements. This similarity appears to indicate a family characteristic since the nature of the curve obtained by plotting the values of $\chi_{ma}$ for the same compounds of thallium (Trew's data), shown in the same figure, is different.

On plotting the values of $\chi_{ma}$ against N for the salts of calcium, strontium and barium containing the same anions, the curves (Fig. 2.) obtained are approximately linear the deviations from linearity are signifcant as they are probably caused by the different effects of similar bonds in different combinations. These lines have been smoothed out in the same manner as followed by Ikenmeyer[9] and the values of $C_1$ and $C_2$ in Ikenmeyer's equation $-\chi_{ma} = C_1 N + C_2$ have been evaluated. These values for different anions

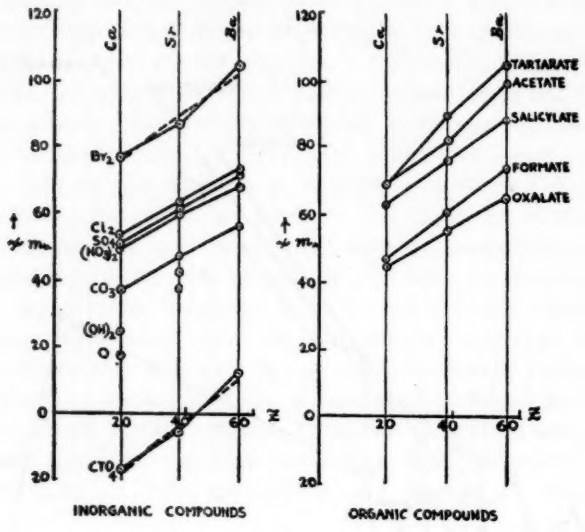


FIG. 2

are given in Table III. Van Vleck[12] has, however, pointed out that 'these linear relations should not be taken too literally as the extrapolation of these lines leads to absurd results.'

TABLE III

| No. | Anions* | $C_1 \times 10^{-6}$ | $C_2 \times 10^{-6}$ |
|---|---|---|---|
| 1 | Oxides | 1·15 | −14·5 |
| 2 | Hydroxides | 1·08 | −19·2 |
| 3 | Fluorides | .. | .. |
| 4 | Carbonates | 0·58 | 9·2 |
| 5 | Chlorides | 0·60 | 21·5 |
| 6 | Oxalates | 0·60 | 10·8 |
| 7 | Formates | 0·75 | − 3·5 |
| 8 | Sulphates | 0·62 | 8·5 |
| 9 | Chromates | 0·55 | −53·7 |
| 10 | Nitrates | 0·55 | 4·0 |
| 11 | Acetates | 0·85 | − 1·0 |
| 12 | Bromides | 0·71 | − 3·0 |
| 13 | Tartrates | 1·00 | −26·5 |
| 14 | Lactates | .. | .. |
| 15 | Salicylates | 0·75 | 91·8 |

* Arranged in the order of increasing N values.

It will be seen from the above table that the values of $C_1$ do not deviate much from the mean and hence it is not unreasonable to infer that the several

lines are approximately parallel to each other. Similar observations have been made by Ikenmeyer[9] which support approximately the Pascal's law of additivity. The mean value of $C_1$ may be statistically interpreted as an increase in the value of $\chi_{ma}$ per unit increase of N, that is the average contribution per electron to the molar susceptibility of any of the salts of calcium, strontium and barium.

The values of $C_2$ differ widely for different salts and do not seem to have any physical meaning.

*Ionic Susceptibility.*—The experimental data is utilised to calculate the ionic susceptibilities of $Ca^{++}$ and $Sr^{++}$, assuming the law of additivity and using all the values of the various anions given by previous workers. These anion values are either (1) taken from the data of previous workers, theoretical or experimental (marked *a*), or (2) deduced from such data by previous workers by appropriate considerations (marked *b*), or (3) deduced on semi-theoretical grounds, such as considerations of the structural formulæ of the anions (marked *c*), or (4) calculated by the authors as mentioned in (2) (unmarked). These values are given in column 4 of the Tables IV and V, and are classified into two parts namely, deduced from the data from (1) solids and (2) solutions. The salts of organic and inorganic acids are considered separately.

Table VI gives the mean values of $\chi_{ma}$ for $Ca^{++}$ and $Sr^{++}$ ions derived from (1) inorganic salts using anion values deduced drom solids, (2) inorganic salts using anion values derived from solutions, (3) organic salts using anion values derived from solids, and (4) organic salts using anion values derived from solutions. The mean in each case is an arithmetic mean as each value is tacitly assumed to be as reliable as any other. A root-mean square value was not taken because the accuracy of the additivity relation is not of such a high order as to warrant it. All the values of $\chi_{ma}$ for $Ca^{++}$ and $Sr^{++}$ ions have been averaged *en masse*. This procedure is slightly different from that adopted in our previous work in which average value of the cation was obtained from every conpound separately; this had an advantage in that each mean cation value could be examined separately with respect to a different molecule, but it is likely to attach undue weight to a set of values.

It appears from the above table that (*i*) the ionic susceptibility of a cation evaluated by using anion values deduced from solution data is less than that obtained when anion values deduced from data on solid salts are used, (*ii*) the cation values deduced from salts of organic acids are higher than those obtained from salts of inorganic acids, both when anion values from solid and solution data are used, and (*iii*) the values calculated according to Slater's and Angus' methods are in fair agreement with the values

TABLE IV

| Compounds | $\chi_{ma}$ Authors | $\chi$ Other ions | | $\chi$ $Ca^{++}$ | |
|---|---|---|---|---|---|
| | | Solid | Solution | Solid | Solution |
| *(a) Values of $\chi_{Ca^{++}}$ ion from calcium salts of inorganic acids* | | | | | |
| $CaBr_2$ .. .. | 76·22 | 30·5 Pascal (*a*)<br>30·64 Pascal (Corrected value)<br>33·9 Hoccart (*a*)<br>36·0 Brindley (*a*)<br>31·4 Farquharson (*a*)<br>31·4 Sugden (*a*)<br>34·7 Kido (*a*)<br>34·5 Hoare & Brindley (*a*)<br>36·29 Prasad (*b*) | 38·3 Joos (*b*)<br>34·8 Ikenmeyer (*a*)<br>32·5 Reicheneder (*a*)<br>34·1 Weiss (*b*)<br>34·1 Abonnec (*a*) | 15·22<br>14·94<br>8·42<br>4·22<br>13·42<br>13·42<br>6·82<br>7·22<br>3·62 | − 0·38<br>6·62<br>11·22<br>8·02<br>8·02 |
| $CaCO_3$ .. .. | 37·37 | 22·2 Pascal (*a*)<br>28·1 Kido (*a*)<br>23·89 Prasad (*b*)<br>18·83 Pascal's values (*c*) | .. | 15·17<br>9·27<br>13·48<br>18·54 | .. |
| $CaCl_2$ .. .. | 53·40 | 20·1 Pascal (*a*)<br>19·85 Bhatnagar & Luther (*a*)<br>23·1 Hoccart (*b*)<br>24·0 Brindley (*a*)<br>20·0 Sugden (*a*)<br>22·1 Kido (*a*)<br>24·2 Hoare & Brindley (*a*)<br>20·6 Prasad (*b*) | 19·5 Joos (*b*)<br>20·4 Ikenmeyer (*a*)<br>21·9 Reicheneder (*a*)<br>23·1 Weiss (*b*)<br>23·9 Weiss (*b*)<br>23·1 Abonnec (*a*)<br>22·2 Leiterer (*a*)<br>22·2 Bhatnagar, Prakash & Hamid (*a*) | 13·2<br>13·7<br>7·2<br>5·4<br>13·4<br>9·2<br>5·0<br>12·21 | 14·4<br>12·6<br>9·6<br>7·2<br>5·6<br>7·2<br>9·0<br>9·0 |
| $CaCrO_4$ .. .. | −16·89 | −35·2 Trew (*a*)<br>−33·0 Trew (*b*)<br>−21·86 Bhatnagar (*b*)<br>−25·70 (*b*)<br>−19·61 Kanekar (*b*) | .. | 18·31<br>16·11<br>4·97<br>8·99<br>2·72 | .. |
| $CaF_2$ .. .. | 26·50 | 5·95 Pascal (*a*)<br>6·3 Pascal (*a*) | 10·8 Joos (*b*)<br>13·9 Ikenmeyer (*a*) | 14·60<br>13·9 | 4·9<br>−1·3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| $CaF_2$ | 26·50 | 5·95 Pascal (*a*)<br>6·3 Pascal (*a*)<br>6·0 Pascal (*a*)<br>12·0 Brindley (*a*)<br>12·2 Kido (*a*)<br>9·4 Hoare & Brindley (*a*) | 10·8 Joos (*b*)<br>13·9 Ikenmeyer (*a*) | 14·60<br>13·9<br>14·5<br>2·5<br>2·1<br>7·7 | 4·9<br>−1·3 |
| $Ca(OH)_2$ | 22·23 | 7·54 Pascal (*a*)<br>7·66 (*c*)<br>7·54 (*c*) | .. | 7·15<br>9·63<br>7·15 | .. |
| $Ca(NO_3)_2$ | 47·10 | 14·2 Pascal (*a*)<br>18·0 Sugden (*a*)<br>20·1 Kido (*a*)<br>18·4 Raichaudhari & Sen Gupta (*a*)<br>18·1 Rao & Sriraman (*a*)<br>16·69 Kanekar (*b*)<br>16·93 (*c*) | 18·4 Reicheneder (*a*)<br>19·5 Rao & Sriraman (*a*) | 8·6<br>11·1<br>6·8<br>10·2<br>10·8<br>13·62<br>13·14 | 10·2<br>8·1 |
| CaO | 15·14 | 4·61 Pascal (*a*) | .. | 5·92 | .. |
| $CaSO_4$ | 48·68 | 33·6 Pascal (*a*)<br>39·0 Kido (*a*)<br>37·0 Trew (*a*)<br>17·34 (*c*)<br>39·13 Kanekar (*b*) | .. | 15·08<br>9·68<br>11·68<br>31·34<br>9·55 | .. |

(*b*) *Values of* $\chi_{Ca^{++}}$ *ion from calcium salts of organic acids*

| | | | | | |
|---|---|---|---|---|---|
| Calcium acetate | 68·40 | 28·9 Pascal (*a*)<br>32·0 Kido (*a*)<br>31·4 Kido (*a*)<br>30·0 Hollens & Spencer (*a*)<br>30·0 Trew (*a*)<br>29·8 Rao & Sriraman (*a*)<br>28·44 Kanekar (*b*)<br>29·62 (*c*)<br>29·26 (*c*) | 30·2 Rao & Sriraman (*a*) | 11·6<br>4·4<br>5·6<br>8·4<br>8·4<br>8·8<br>11·53<br>8·16<br>9·88 | 8·0 |
| Calcium formate | 45·30 | 16·9 Pascal (*a*)<br>20·2 Kido (*a*)<br>17·3 Rao & Sriraman (*a*)<br>15·54 Kanekar (*b*)<br>17·27 (*c*)<br>17·15 (*c*) | 17·6 Rao & Sriraman (*a*) | 11·5<br>4·9<br>10·7<br>14·22<br>10·76<br>11·0 | 10·1 |

TABLE IV—(*Contd.*)

| Compounds | $\chi_{ma}$ Authors | $\chi$ Other ions | | $\chi Ca^{++}$ | |
|---|---|---|---|---|---|
| | | Solid | Solution | Solid | Solution |
| Calcium lactate .. | 122·70 | 53·92 (*c*)<br>53·44 (*a*) | .. | 14·86<br>15·82 | .. |
| Calcium oxalate .. | 44·30 | 27·94 Pascal (*a*)<br>28·5 Hollens & Spencer (*a*)<br>22·15 Kanekar (*b*)<br>22·19 (*c*) | .. | 16·36<br>15·8<br>22·15<br>22·11 | .. |
| Calcium salicylate .. | 162·02 | 71·44 Pascal (*a*)<br>72·71 Prasad (*b*)<br>74·68 (*c*) | .. | 20·14<br>16·60<br>12·66 | .. |
| Calcium tartrate .. | 68·36 | 62·36 Pascal<br>63·8 Trew<br>61·52 Prasad (*b*)<br>60·88 | .. | 6·0<br>4·56<br>6·84<br>13·48 | .. |

TABLE V

| Compounds | $\chi_{ma}$ Authors | $\chi$ Other ions | | $\chi$ $Sr^{++}$ | |
|---|---|---|---|---|---|
| | | Solid | Solution | Solid | Solution |
| *(a) Values of $\chi_{Sr^{++}}$ ions from strontium salts of inorganic acids* | | | | | |
| $SrBr_2$ .. .. | 86·30 | 30·5 Pascal (*a*)<br>30·64 Pascal (Corrected value)<br>33·9 Hoccart (*a*)<br>36·0 Brindley (*a*)<br>31·4 Farquharson (*a*)<br>31·4 Sugden (*a*)<br>34·7 Kido (*a*)<br>34·5 Hoare & Brindley (*a*)<br>36·29 Kanekar (*b*) | 38·3 Ioos (*b*)<br>34·8 Ikenmeyer (*a*)<br>32·5 Reicheneder (*a*)<br>34·1 Weiss (*b*)<br>34·1 Abonnec (*a*) | 25·63<br>25·35<br>18·83<br>14·63<br>23·83<br>23·83<br>17·23<br>17·63<br>14·03 | 10·03<br>17·03<br>21·63<br>18·43<br>18·43 |
| $SrCO_3$ .. .. | 47·23 | 22·2 Pascal (*a*)<br>28·1 Kido (*a*)<br>23·89 Kanekar (*b*)<br>18·83 Pascal's value (*c*) | .. | 25·03<br>19·13<br>23·34<br>28·4 | .. |
| $SrCl_2$ .. .. | 63·60 | 20·1 Pascal (*a*)<br>19·85 Bhatnagar & Luther (*a*)<br>23·1 Hoccart (*b*)<br>24·0 Brindley (*a*)<br>20·0 Sugden (*a*)<br>22·1 Kido (*a*)<br>24·2 Hoare & Brindley (*a*)<br>20·6 Kanekar (*b*) | 19·5 Ioos (*b*)<br>20·4 Ikenmeyer (*a*)<br>21·9 Reicheneder (*a*)<br>23·1 Weiss (*b*)<br>23·9 Weiss (*b*)<br>23·1 Abonnec (*a*)<br>22·2 Leiterer (*a*)<br>22·2 Bhatnagar, Prakash & Hamid | 23·4<br>23·82<br>17·4<br>15·6<br>23·6<br>19·14<br>15·2<br>22·41 | 24·6<br>22·8<br>19·8<br>17·4<br>16·8<br>17·4<br>19·2<br>19·2 |
| $SrCrO_4$ .. .. | −5·09 | −35·2 Trew (*a*)<br>−33·0 Trew (*b*)<br>−21·86 Bhatnagar, Prakash & Hamid<br>−24·7 (*b*) (*b*)<br>−19·61 Kanekar (*b*) | .. | 30·11<br>27·91<br>16·77<br>20·61<br>14·52 | .. |
| $Sr(OH)_2$ .. .. | 40·40 | 7·54 Pascal (*a*)<br>7·66 (*c*)<br>7·54 (*c*) | .. | 25·32<br>25·08<br>25·32 | .. |

| | | | | | | |
|---|---|---|---|---|---|---|
| $SrSO_4$ .. .. | 60·30 | 33·6 Pascal (*a*)<br>39·0 Kido (*a*)<br>37·0 Trew (*a*)<br>17·34 Trew (*c*)<br>39·13 Kanekar (*b*) | .. | | 26·70<br>21·3<br>23·3<br>42·96<br>21·17 | .. |
| $Sr(NO_3)_2$ .. .. | 57·86 | 14·2 Pascal (*a*)<br>18·0 Sugden (*a*)<br>20·1 Kido (*a*)<br>18·4 Raichaudhari & Sen-Gupta (*a*)<br>18·1 Rao & Sriraman (*a*)<br>16·69 Kanekar (*b*)<br>16·93 (*c*) | 18·4 Reicheneder (*a*)<br>19·5 Rao & Sriraman (*a*) | | 29·46<br>21·86<br>17·66<br>21·06<br>21·66<br>24·48<br>24·00 | 21·06<br>18·86 |
| SrO .. .. | 35·22 | 4·61 Pascal (*a*) | .. | | 30·61 | .. |

*(b) Values of $\chi_{Sr^{++}}$ ions from Strontium salts of organic acids*

| | | | | | | |
|---|---|---|---|---|---|---|
| Strontium acetate .. | 81·22 | 28·9 Pascal (*a*)<br>32·0 Kido (*a*)<br>31·4 Kido (*a*)<br>30·0 Hollens & Spencer (*a*)<br>30·0 Trew (*a*)<br>29·8 Rao & Sriraman (*a*)<br>28·44 Kanekar (*b*)<br>29·62 (*c*)<br>29·26 (*c*) | 30·2 Rao & Sriraman (*a*) | | 23·42<br>17·22<br>18·42<br>21·22<br>21·22<br>21·62<br>24·35<br>21·98<br>22·70 | 21·82 |
| Strontium oxalate .. | 54·64 | 27·94 Pascal (*a*)<br>28·5 Hollens & Spencer (*a*)<br>22·15 Kanekar (*b*)<br>22·19 (*c*) | .. | | 26·7<br>26·14<br>32·49<br>32·45 | .. |
| Strontium formate .. | 60·30 | 16·9 Pascal (*a*)<br>20·2 Kido (*a*)<br>17·3 Rao & Sriraman (*a*)<br>15·54 Kanekar (*b*)<br>17·27 (*c*)<br>17·15 (*c*) | 17·6 Rao & Sriraman (*c*) | | 26·5<br>19·9<br>25·7<br>29·22<br>25·76<br>26·00 | 25·1 |
| Strontium salicylate .. | 176·28 | 71·44 Pascal (*a*)<br>72·71 Kanekar (*b*)<br>74·63 (*c*) | .. | | 33·4<br>30·86<br>26·92 | .. |
| Strontium tartrate .. | 88·66 | 62·36 Pascal<br>63·8 Trew<br>61·52 Kanekar (*b*)<br>60·88 | ..<br>.. | | 26·3<br>24·86<br>27·14<br>17·78 | .. |

TABLE VI

| Source | $\chi_{ms}$ for $Ca^{++}$ | $\chi_{ms}$ for $Sr^{++}$ |
|---|---|---|
| (1) | 10·65 | 22·61 |
| (2) | 7·65 | 18·85 |
| (3) | 12·33 | 26·36 |
| (4) | 9·05 | 23·46 |
| Slater | 11·2 | 27·1 |
| Angus | 10·42 | 32·1 |

obtained in this investigation using anion values deduced from solid salts. The same observations have been made by Trew (11) and Prasad and co-workers.[1] In view of the important implications of the first two observations and since the numbers of the samples used for the different averages are different, the observed results were statistically examined by the usual formula for standard deviations, and it was confirmed that the observed differences in the two cases are significant.

Trew[11] and Prasad and co-workers[1] have observed that the ionic susceptibilities of cations calculated from the susceptibilities of their compounds with organic acids increase with the increase in the number of carbon atoms in the compounds. Trew has suggested that the increase in the number of carbon atoms in the compounds increases the size of the negative ions and this causes an increase in the effective ionic radius of the cation and hence an increase in the susceptibility of that ion. Looking to the importance of these observations, the data obtained on the susceptibilities of calcium and strontium salts of organic acids were also examined from the aforesaid point of view and the results obtained are given in the following table. The susceptibility values of anions used in calculating the values $\chi$ cation given in the last column of Table VII are the mean of the values given in column 5 under 'solid' in Tables IV and V.

TABLE VII

| Compound | No. of carbon atoms | N | $\chi_{ms}$ (obs.) | $\chi$ cation |
|---|---|---|---|---|
| Calcium Oxalate .. .. .. | 2 | 64 | 44·30 | 19·10 |
| ,, Formate .. .. .. | 2 | 66 | 45·30 | 10·52 |
| ,, Acetate .. .. .. | 4 | 82 | 68·40 | 8·52 |
| ,, Tartrate .. .. .. | 4 | 96 | 68·36 | 12·28 |
| ,, Lactate .. .. .. | 6 | 150 | 122·7 | 15·34 |
| ,, Salicylate .. .. .. | 14 | 150 | 162·02 | 16·14 |
| Strontium Oxalate .. .. .. | 2 | 82 | 54·64 | 29·44 |
| ,, Formate .. .. .. | 2 | 84 | 60·30 | 25·52 |
| ,, Acetate .. .. .. | 4 | 100 | 81·22 | 21·34 |
| ,, Tartrate .. .. .. | 4 | 114 | 88·66 | 32·54 |
| ,, Salicylate .. .. .. | 14 | 168 | 176·28 | 30·40 |

Two facts emerge out from the results given above: (*i*) there is no steady increase in the value of $\chi$ cation with increasing values of either N or the number of carbon atoms, and (*ii*) there is a definite increase in the values of $\chi_{ma}$ with an increase in both N and the number of carbon atoms. These results are not exactly the same as those obtained by previous workers. It is therefore necessary that some more salts of organic acids should be examined in order to arrive at some definite conclusions. Experiments based on these lines are being carried out in this laboratory.

*Electronic isomers.*—The results obtained in this investigation have been compared also with those calculated according to the theory of electronic isomers suggested by Bhatnagar and Mathur,[13] who empirically generalising the Langevin-Pauli formula obtained:

$$\chi_{ma} = -\frac{Le^2}{6mc^2} K r^2 = -2{\cdot}832 \times 10^{10} K r^2$$

in which the numerical value of K is the same for electronic isomers.

For this purpose the values of K were calculated from (1) the known values of $\chi_{ma}$ obtained from the *International Critical Tables* (1929) and *Landolt-Bornstein's Physikalischechemischen Tabellen* (1936) for a set of the electronic isomers of compounds studied in this investigation, and (2) the values of $r$ calculated on the basis of Bragg's theory of closest packing using Bragg's data as done by Bhatnagar and Mathur, from the relation:

$$K = -\chi_{ma}/2{\cdot}832 \times 10^{10} r^2.$$

Using these values of K and values of $r$ calculated as stated above, the values of $\chi_{ma}$ for salts studied in this investigation were calculated and they are given in Table VIII.

It can be seen from Table VIII that there are large differences between the calculated values and the values obtained by the authors and other workers (*cf.* last column of the table). The disagreement between the calculated and the observed values cannot be accounted for by correcting the values of $r$ only; it appears that some other factors have to be taken into account to reproduce the experimental results.

*Ionic radius.*—From the mean ionic susceptibilities of $Ca^{++}$ and $Sr^{++}$ their ionic radii have been calculated and are compared with the values obtained by other workers. The results obtained are shown in Table IX.

It appears from Table IX that the authors' calculated values are in better agreement with those of Slater.

TABLE VIII

| Isomer | | | | Compound studied | | | | |
|---|---|---|---|---|---|---|---|---|
| Name | R (A.U.) | $\chi_{ms}$ | K | Name | R (A.U.) | $\chi_{ms}$ (cal.) | $\chi_{ms}$ (obs.) | $\chi_{ms}$ (obs.) by others (*cf.* Table I) |
| $BaCl_2$ | 2·262 | 85·3 | 5·89 | $CaBr_2$ | 2·023 | 68·25 | 76·22 | 54·55 |
| ,, | | 73·50* | 5·10 | ,, | | 58·9 | | |
| $Al_2O_3$ | 1·791 | 9·98 | 1·1 | $CaCO_3$ | 1·836 | 10·46 | 37·37 | 38·2 |
| $KNO_3$ | 2·152 | 32·95 | 2·52 | ,, | | 24·0 | | 14·01 |
| | 2·156† | | 1·7† | | | 13·28† | | 35·5 |
| | | | | | | | | 40·08 |
| | | | | | | | | 37·8 |
| $BeCl_2$ | 1·566 | 47·9 | 6·90 | $CaF_2$ | 1·726 | 58·3 | 26·50 | 23·4 |
| $CS_2$ | 1·371 | 41·12 | 7·70 | ,, | | 64·9 | | 15·6 |
| | | | | | | | | 22·25 |
| | | | | | | | | 28·1 |
| $N_2O_5$ | 2·877 | 15·65 | 0·67 | $Ca(OH)_2$ | 1·793 | 6·08 | 22·23 | 28·9 |
| | | | | | | | | 21·3 |
| NaCl | 2·825 | 29·2 | 1·29 | CaO | 2·350 | 20·2 | 15·14 | 15·13 |
| | | 23·98† | 1·0† | | | 15·74† | | 15·74 |
| $K_2CO_3$ | 2·671 | 67·4 | 3·345 | $CaSO_4$ | 1·919 | 34·75 | 48·68 | 51·8 |
| | 2·675† | 66·02† | 3·26 | | 1·922† | 34·1† | | 42·54 |
| | | | | | | | | 49·6 |
| | | | | | | | | 46·34 |
| | | | | | | | | 51·73 |
| | | | | | | | | 46·8 |
| $RbNO_3$ | 2·320 | 41·4 | 2·72 | $SrCO_3$ | 2·056 | 32·53 | 47·23 | 46·60 |
| | | | | | | | | 25·25 |
| | | | | | | | 29·18† | 44·2 |
| NaBr | 1·934 | 48·3 | 3·62 | SrO | 1·973 | 39·9 | 35·22 | 61·88 |
| | | | | | | | | 25·04 |
| $Rb_2CO_3$ | 2·887 | 74·09 | 3·14 | $BaSO_4$ | 2·258 | 45·3 | 71·44 | |

* The observed value of $BaCl_2$ is here taken as the basis for calculation.
† Values given by Bhatnagar and Mathur.

TABLE IX

| Ion | Authors' calculated values | Values of other workers | |
|---|---|---|---|
| | | Wassastjerna | Slater |
| | Å | Å | Å |
| $Ca^{++}$ (inorganic) .. .. | 1·21 | 1·02 | 1·17 |
| $Ca^{++}$ (organic) .. .. | 1·29 | — | — |
| $Sr^{++}$ (inorganic) .. .. | 1·31 | 1·20 | 1·43 |
| $Sr^{++}$ (organic) .. .. | 1·41 | — | — |

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# THE ANGULAR DIVERGENCE OF THE X-RAY REFLECTIONS BY DIAMOND

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## 1. *Introduction*

It is a fairly well-known fact that the geometric character of the X-ray reflections given by diamond varies from crystal to crystal. Mark (1925) found that, with the best specimens, the crystal reflecton is so perfect that the MoK$\alpha_1$ and K$\alpha_2$ radiations can be photographed beautifully at a distance of 10 metres. On the other hand, certain other specimens were so bad that the X-ray lines were not resolved at all. Ehrenberg, Ewald and Mark (1928) found by means of the double spectrometer that some specimens give extraordinarily precise reflections, while others were far inferior in this respect. However, these workers made no attempt to correlate the X-ray effects with the other properties of diamond. Recently, Lonsdale (1942) found that diamonds of the ultra-violet transparent type give much more intense X-ray reflections than those which are opaque to the ultra-violet, indicating a greater mosaicity in the structure of the former. Krishnan (1944) and Hariharan (1944) have studied this aspect more thoroughly, and have found that, among the opaque diamonds, which fluoresce blue, the intensity of X-ray reflection steadily increases with the intensity of fluorescence, a result which becomes intelligible on the idea (Raman, 1944) that diamonds of the ultra-violet opaque variety consist of the positive and the negative tetrahedral structures interpenetrating each other, and that the intensity of fluorescence is greater the more intimately the two structures are intermixed.

In the present paper, an investigation of the angular divergence of the X-ray reflection given by different diamonds is reported. The method consists in obtaining the reflection of the MoK$\alpha_1$ and K$\alpha_2$ radiations from the surface (111) planes of a stationary crystal, using a fine slit, and measuring the widths of the lines registered on a photographic film kept at a large distance from the crystal. Allowing for the lack of monochromatism of the incident X-ray, and the consequent divergence arising from this cause, it is possible to calculate the actual divergence of a monochromatic reflection

given by the crystal. It is clearly found that, in blue-fluorescent diamonds which are fairly free from birefringence, the divergence is greater, the larger is the intensity of fluorescence.

### 2. *Experimental Arrangement*

The apparatus employed was very simple, being similar to that used by the author (1944) in his investigation of the X-ray topographs of diamond. A fine lead slit, about 0·07 mm. in width and 1 mm. in height, placed in front of the window of a molybdenum target X-ray tube, was the source of X-rays. At a distance of 6·5 cm. from the slit was placed a two-circle goniometer, on which the crystal was to be mounted. The goniometer was so adjusted that its vertical axis was accurately parallel to the height of the slit. The crystal of diamond, in the form of an octahedral cleavage plate, was mounted on the goniometer such that its surface (111) planes were exactly in the vertical plane, and were parallel to the vertical axis of rotation of the goniometer. By trial, the crystal was set so that the characteristic MoK$\alpha$ line appeared in the distorted 111 X-ray topograph given by the crystal on a film kept normal to the incident beam at a distance of about 3 cm. from the crystal. Then the film was moved away to a distance of 40 cm. from the crystal, and was kept normal to the reflected beam. The MoK$\alpha_1$ and K$\alpha_2$ lines were then obtained clearly resolved. A series of pictures were taken with suitable exposures with the film at distances of 20, 40, 60, 80 and 120 cm. from the crystal, for reasons to be explained in a later section. The exposures were adjusted so that the image obtained on the film was just clearly visible, so as to avoid any spreading of the image. No intensifying screen was used, and the development was always carried out in developers made from the same stock solution, and for a standard time of $1\frac{1}{2}$ minutes. In this way, the reflections were recorded with four blue-fluorescent diamonds, exhibiting varying intensities of blue fluorescence, which were carefully chosen from Prof. Sir C. V. Raman's collection.

It may be remarked here that the method employed in the present experiment is similar to that used by Mark (*loc. cit.*), and by Valasek (1930) in his investigation on the fine-structure of X-ray lines. Mark used a pinhole as the source. The advantage of using a fine slit is that the width of the slit can be reduced without appreciable loss in intensity, for the height can be increased. Of course, there is an upper limit to the height on account of the fact that it has a detrimental effect on the sharpness of the line on the film. Under the conditions of the present experiment, however, it can easily be shown that the broadening so produced is negligible, being only of the order of 0·001 mm. at a distance of 50 cm. and less at larger distances.

### 3. *Theory of the Experiment*

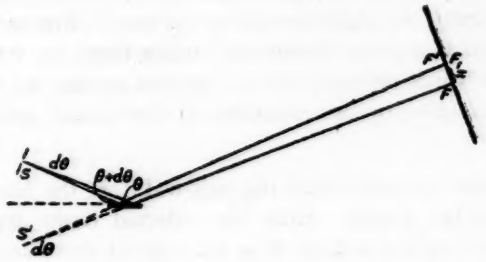


FIG. 1. X-Ray Reflection from a Stationary Crystal

Fig. 1 represents a horizontal cross-section of the experimental arrangement. S is the slit, which is the source of X-rays, and FF' is the photographic film, placed normal to the reflected beam at a large distance from the crystal. Suppose that the crystal were such that it gives a reflection only at the precise Bragg angle ($\theta$ say), and further assume that the X-rays are strictly monochromatic. It is then obvious from Fig. 1 that, if the crystal were oriented properly, then the width of the reflected line obtained on the film at F would be equal to the width of the slit, and would be independent of the distance of the film from the crystal.

Actually, neither of the above two conditions is satisfied. The Bragg reflection for a monochromatic beam takes place over a finite range of angles, and besides, the X-ray line (the MoK$\alpha_1$ or K$\alpha_2$ say) covers a small range of wave-lengths. The effect of both of these is to produce a divergence of the reflected beam, and as will be obvious from Fig. 1, if $d\theta$ is the range of angles over which the reflection occurs, the reflected beam would have a divergence equal to this, and would appear to diverge from a point S', which is the image of S in the plane of the crystal. The width of the line obtained on the film would, therefore, be greater than the width of the slit, and it would increase with increasing distance of the film from the crystal.

The above is the case with a perfect crystal. Now, suppose that the crystal possesses a certain amount of mosaic structure, *i.e.*, it consists of a large number of blocks which are slightly disoriented with respect to one another. It is then obvious that the Bragg reflection can occur over a wider range of angles than with a perfect crystal, and that the reflected beam would consequently be more divergent. It may also be remarked in this connection that a variation of the lattice spacing of the crystal would also produce precisely the same effect. In fact, such a variation of lattice spacing cannot be distinguished from the presence of mosaic structure by

the present experimental technique. What one can determine is only the magnitude of the resulting divergence, which may be due to either cause, or both. Consequently, we shall denote by the term '*divergence* of the crystal reflection,' the total angular divergence arising from the finite width of the Bragg reflection which occurs even in a perfect crystal, as well as from the presence of mosaicity or a variation in the lattice spacing as the case may be.

We shall now consider what the half-width of the line would be at a distance R from the source. Since the reflected beam appears to diverge from the image S′ of the source, R is the sum of the distance of the film from the crystal, and that of the crystal from the slit. The intensity distribution in the line has a shape similar to that of a Gaussian error curve, as will be seen below. The term " half-width " consequently stands for the half-width at half-maximum.

Ever since the classical work of Ehrenberg, Ewald and Mark (1928) on the width of X-ray reflection, it is customary to represent the reflection curve for a perfect crystal in the form

$$I_\phi = \exp\left[-(\phi^2/c^2)\log 2\right] \tag{1}$$

where $\phi$ is the angular departure from the Bragg angle corrected for refractive index, and $c$ is the half-width at half maximum. In the same way, for an imperfect crystal, we shall represent the variation of the intensity of the reflected beam with angle in the form

$$I_\phi = \exp\left[-\phi^2(\log 2)/w^2\right] \tag{2}$$

where $\phi$ is the angle measured from that for which I is a maximum, and $w$ is the half-width of the " divergence." We shall not consider in this section the relation between $w$ and the half-width of a perfect crystal reflection $c$.

Now, the X-ray line also has a distribution of intensity of the form

$$I_\lambda = \exp\left[-(\lambda-\lambda_0)^2(\log 2)/w_\lambda^2\right] \tag{3}$$

where $\lambda_0$ is the wavelength of maximum intensity, and $w_\lambda$ is the half-width at half-maximum. If D is the dispersion $(d\phi/d\lambda)$ of the crystal for the wavelength concerned $(\lambda_0)$, then it is easily seen that the angular variation of the intensity in the reflected beam is given by

$$I_\phi = \exp\left[-\phi^2(\log 2)/(w^2 + D^2 w_\lambda^2)\right] \tag{4}$$

where $\phi$ is the angle measured from that for which the intensity is a maximum. Putting $Dw_\lambda = l$, the half-width at half-maximum is equal to $(w^2 + l^2)^{\frac{1}{2}}$. Denoting this by W,

$$W = \sqrt{w^2 + l^2} \tag{5}$$

We shall now derive an expression for the half-width $a$ of the line on a film kept at a distance R from the source in terms of W and the width of the slit $2b$. For this, we follow a procedure analogous to that employed in a theory, first given by Allison (1931), for an arrangement slightly different from ours. If F be the centre of the line on the film (Fig. 1), and if we consider a point $F_1$ at a distance $x$ from it, then the intensity at $F_1$ is given by

$$I_x = \int_{\frac{x}{R}-\frac{b}{R}}^{\frac{x}{R}+\frac{b}{R}} e^{-(\phi^2/w^2)\log 2}\, d\phi. \tag{6}$$

Put $(x/R) \div (W/\sqrt{\log 2}) = X$ and $(b/R) \div (W/\sqrt{\log 2}) = B$. Then,

$$I_x = \int_{X-B}^{X+B} e^{-\phi^2}\, d\phi. \tag{7}$$

This gives the intensity distribution of the line on the plate, and its half-width $a$ can be determined by plotting the value of the integral (6) as was done by Allison. The elaborate procedure of plotting graphs can, however, be avoided, and the half-width can be determined with greater accuracy by the method described below. One has only to make use of a table of the error integral

$$Ei(z) = \int_{\bullet}^{z} e^{-\phi^2}\, d\phi. \tag{8}$$

First determine $I_0 = 2Ei(B)$, and then find from the tables the value of X, for which $Ei(X + B) - Ei(X - B) = I_0/2 = Ei(B)$. This can easily be done by interpolation. In this way, the half-width of the line has been evaluated for various values of B, and the results are tabulated in Table I. The actual quantities given in the table are those that would be needed in calculations with the observed values. A is $= a/R$, D is $= b/R$, and W has the same significance as before. The various ratios of these quantities are given in Table I, since they alone come in, in the numerical computations.

Making use of this table, it is a simple matter to determine the half-width of the divergence $w$ from the measured value of $a$, knowing the slit-width $2b$. One has only to find the ratio $a/b$, which is equal to A/D, and then find the corresponding value of A/W. The magnitude of W is then known, and from (5), $w$ can be calculated, knowing $l$.

### 4. *Technique of Measurement*

In actual practice, it is not possible to apply directly the theory described in the previous section for the evaluation of the divergence of the crystal

TABLE I

| D/W | A/W | A/D | D/W | A/W | A/D |
|---|---|---|---|---|---|
| 0·120 | 1·003 | 8·35 | 1·500 | 1·581 | 1·054 |
| 0·240 | 1·014 | 4·22 | 1·562 | 1·631 | 1·045 |
| 0·500 | 1·059 | 2·12 | 1·682 | 1·732 | 1·030 |
| 0·601 | 1·086 | 1·81 | 1·802 | 1·838 | 1·020 |
| 0·721 | 1·126 | 1·56 | 1·922 | 1·947 | 1·014 |
| 0·841 | 1·173 | 1·395 | 2·042 | 2·060 | 1·009 |
| 0·961 | 1·228 | 1·280 | 2·162 | 2·174 | 1·006 |
| 1·000 | 1·247 | 1·247 | 2·282 | 2·291 | 1·004 |
| 1·081 | 1·294 | 1·197 | 2·402 | 2·406 | 1·002 |
| 1·201 | 1·367 | 1·138 | 2·523 | 2·525 | 1·001 |
| 1·321 | 1·448 | 1·096 | 2·763 | 2·764 | 1·0005 |
| 1·442 | 1·537 | 1·066 | 3·003 | 3·003 | 1·0002 |

reflection from the measured width. This is because a microphotometer has to be employed for the measurement of the half-width of the phtographic line, and the microphotometric spot which scans the line has a finite width. This brings in complications, and the half-width deduced from the microphotometric trace has to be corrected for this. It is obvious that it is not possible to carry out the correction in an exact manner, since too many unknown quantities come in. In the present experiment, the following approximate method was employed.

It was assumed that the effect of the microphotometry is merely to increase the effective width of the slit. In other words, the broadening produced by the instrument could be represented as equivalent to an increase in the width of the slit. Consequently, the width $2b$ of the slit in the formulæ in section 3 should be replaced by another quantity $2b'$ which may be called the " effective width " of the slit, and which has to be determined. It was for this purpose that a number of photographs were taken with each diamond at different distances.

The method of determining the effective width was as follows. As a first approximation, the half-width measured from the microphotometric trace of the line at the shortest distance, *i.e.*, 20 cm., was taken to be equal to half the effective width. This is justified because, for this distance, $a$/R

was actually of the order of $2 \cdot 5 \times 10^{-5}$, and the half-width W even for the most intensely fluorescent diamond was $1 \cdot 1 \times 10^{-5}$, so that A/W was $> 2$, and A/D was less than $1 \cdot 01$. Thus, the error introduced by taking the half-width of the line $a$ to be equal to $b'$ was less than 1%. With this value for the effective slit-width, the magnitude of W was deduced from the measurement of the line-widths at other distances as an average. For the least fluorescent diamonds, N.C. 72 and 73, the individual values varied by as much as 20%, but for the other two diamonds examined, N.C. 62 and 81, the variation was much less, being less than 10%. No systematic variation with distance occurred in any of these cases, showing that the effective width is practically a constant.

A second approximation was also worked out for one of the diamonds by using the mean value of W, and the measured half-width at 20 cm., and then evaluating the effective slit-width from these. The correction so introduced was less than 1%, and since the individual variations due to the errors of measurement far exceeded this value, it was not thought worthwhile to apply this correction. The validity of the approximation was also shown by the fact that the half-width $a$ at 20 cm. was the same for all the four diamonds for which the value of W varied from 8 to 20 seconds, and also for both the $K\alpha_1$ and the $K\alpha_2$ lines.

The distance of the film from the source was not determined by direct measurement, but was deduced from the measured separation of the $K\alpha_1$ and $K\alpha_2$ components, the wavelength difference between which is accurately known. This had the advantage that any errors due to the shrinkage of the film, etc., were automatically corrected for. The half-width of the photographic line was obtained from the microphotometric trace after converting it into a curve showing *the intensity plotted against distance*, and then determining the width at half-maximum. This was done for both the $K\alpha_1$ and the $K\alpha_2$ lines, and incidentally, it was verified that the $K\alpha_2$ intensity was very nearly half that of the $K\alpha_1$, the mean of the measured values being 0·493 (*cf.* Williams, 1933).

The magnitude of $w$, the half-width of the crystal reflection was deduced by using the relation

$$W^2 = w^2 + l^2,$$

derived in section 3. The width of the X-ray line was taken from the results of Allison and Williams (1930). $2w_\lambda = 0 \cdot 29$ X.U. for Mo. $K\alpha_1$ and $= 0 \cdot 32$ X.U. for Mo$K\alpha_2$. The corresponding values of $l$ for diamond are $3 \cdot 58 \times 10^{-6}$ and $3 \cdot 95 \times 10^{-6}$.

Typical intensity curves for the line at 86·5 cm. with the four diamonds that were studied are reproduced in Fig. 2. The distance between the short vertical lines in these indicates the effective width of the slit. The mean

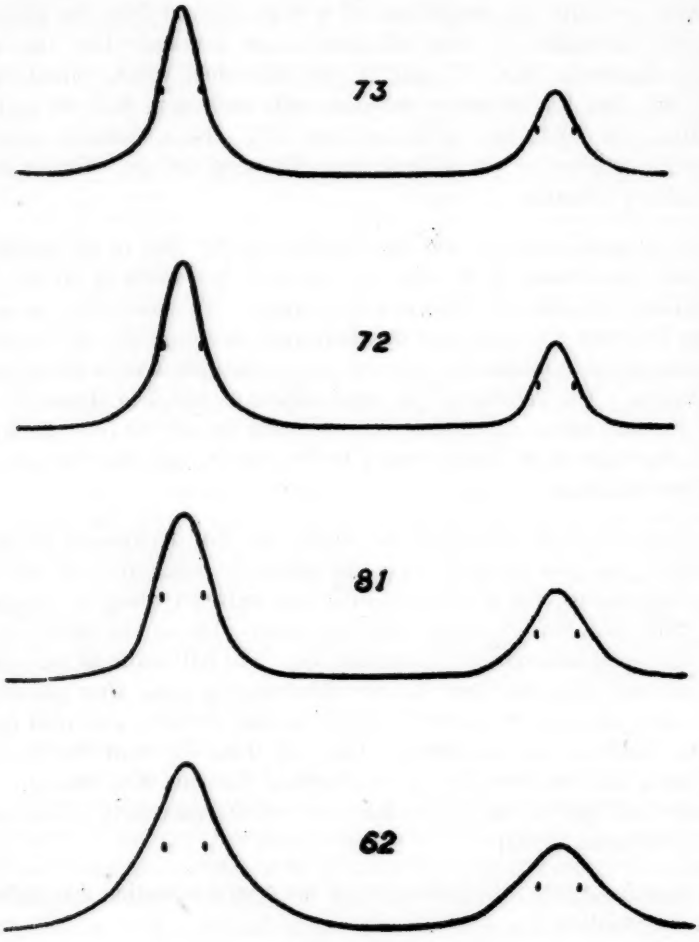


FIG. 2. Intensity Curves for Four Diamonds

values of W and $w$ are collected in Table II below. An estimate of the relative intensity of fluorescence is also given in the last column.

TABLE II

| Diamond N.C. | Mean value of W in radians | | $w$ in radians | | | $w$ in seconds | $m$ in seconds | Relative intensity of Fluorescence |
|---|---|---|---|---|---|---|---|---|
| | $K\alpha_1$ | $K\alpha_2$ | $K\alpha_1$ | $K\alpha_2$ | Mean | | | |
| 73 | $3{\cdot}78\times10^{-6}$ | $4{\cdot}20\times10^{-6}$ | $1{\cdot}22\times10^{-6}$ | $1{\cdot}43\times10^{-6}$ | $1{\cdot}3\times10^{-6}$ | 2·7 | 1·9 | 1·0 |
| 72 | 4·26 | 4·62 | 2·31 | 2·39 | 2·35 | 4·8 | 4·3 | 4·1 |
| 81 | 7·51 | 7·88 | 6·60 | 6·82 | 6·7 | 13·8 | 13·8 | 23 |
| 62 | 11·07 | 11·07 | 10·47 | 10·34 | 10·4 | 21·4 | 21·4 | 990 |

This was obtained by photographic photometry of the fluorescence intensity. All the four diamonds were placed in a beam of ultra-violet light from a source of constant intensity, and were photographed by fluorescent light, using a filter of sodium nitrite solution to cut off the ultra-violet. A series of photographs with varying exposures from 2 seconds to 45 minutes were taken, and the density of the images on the plate was obtained by a microphotometer. By interpolation, the exposure necessary for each of the diamonds to give an image of a certain density was determined, and the reciprocal of this quantity gave a reasonable estimate of the relative intensities of fluorescence.

### 5. *Interpretation of the Results*

The results described in the previous section make it very clear that the more intensely blue-fluorescent a diamond is, the greater is the angular divergence of the crystal reflection. Now, it is well known that even for a perfect crystal, the monochromatic reflected beam has a finite angular divergence, the half-width of which is $c$ (Eq. 1). Any increase in the divergence must therefore be attributed to the presence of discontinuities in the lattice structure. As already said, this may be in the form of a mosaic structure *i.e.,* the crystal may consist of a large number of mosaic crystallites, which are slightly tilted with respect to one another, or there may be some irregularities in the spacing of the atomic planes, without any angular tilting, which also has the effect that the crystal reflection occurs for a range of angles larger than that for a perfect crystal. In the former case, we may consider the angular distribution of the mosaic blocks to be of the form

$$n(\alpha) = \exp[-(\log 2)(\alpha^2/m^2)], \tag{9}$$

where $\alpha$ is the inclination of a block to the mean orientation, and $m$ is that value of $\alpha$, for which $n(\alpha)$ is half the maximum, *i.e.,* $n(0)$. It is then easily

verified that the half-width of the crystal reflection, $w$, is given by

$$w^2 = c^2 + m^2 \tag{10}$$

The same result holds also in the case of a variation in lattice spacing ; but $m$ here represents the half-width of the divergence of the reflected X-ray beam resulting from such a variation. In either case, $m$ obviously gives one an idea of the departure from perfection of the crystal. Its magnitude is also included in Table II. This was calculated from $w$, making use of the theoretical value of $c$ as calculated from Ewald's theory (see Ehrenberg *et al* 1928) *viz.*, $0{\cdot}96 \times 10^{-6}$.

It is interesting to compare the magnitude of $m$ with that of the intensity of fluorescence F. In Fig. 3, $m$ has been plotted against log F. It will be seen from the figure that the deviation from perfection is very small for small intensities of fluorescence, then increases rapidly, finally reaching a saturation value for high intensities of fluorescence.

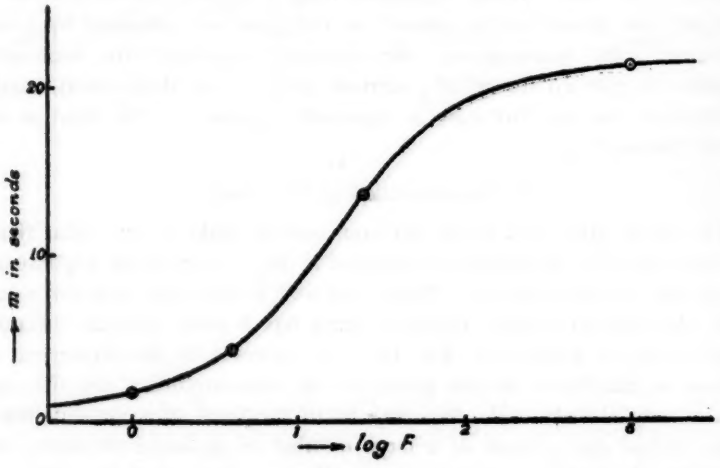


FIG. 3. Curve showing relation between fluorescence intensity and crystal perfection

We shall now consider the relation between the divergence of crystal reflection and the integrated intensity of the Bragg reflection. Considering a monochromatic X-ray, it is clear that with a perfect crystal the reflected beam would have a half-width equal to $c$. In an imperfect crystal, however, the reflection would occur over a wider range of angles, and the reflected beam would have a half-width $w$, greater than $c$. The integrated intensity

would consequently be proportional to

$$\int_{-\infty}^{+\infty} e^{-(\log 2)\,(\phi^2/w^2)}\, d\phi = w\sqrt{\pi} \qquad (11)$$

This is true for every monochromatic component of the X-ray, so that the integrated reflection is directly proportional to $w$. Now, from Table II, the ratio of the values of $w$ for the two diamonds N.C. 81 and 72 is 2·85. Hariharan (*loc. cit.*) who studied the integrated intensity of the Bragg reflection, finds that the ratio for the same two diamonds, D 41 and D 45 respectively, is 3·2. The two are in satisfactory agreement, considering the limits of experimental error. As far as the author is aware, this relation between the integrated intensity and the width of X-ray reflection does not seem to have been verified by anybody previously.

It is interesting to note that in N.C. 73, the most perfect of the diamonds examined, the half-width of the divergence is very nearly the same as the theoretical value, being equal to $1{\cdot}3 \times 10^{-6}$, as compared with $0{\cdot}96 \times 10^{-6}$, given by Ewald's theory.

A remark is here necessary on the statement made by Allison (1931) on Valasek's (1930) determination of the width of X-ray lines by the photographic method, employing an experimental arrangement similar to the author's. Commenting on the fact that Valasek's value is appreciably greater than that obtained by the double spectrometer method, Allison remarks that the photographic method is unreliable since a lateral spreading of the image occurs owing to the scattering in the photographic film. That such an effect, if it exists, can be reduced to negligible proportions is shown by the present experiment. Here, special care was taken to obtain the photograph with the least density necessary to obtain measurable microphotometric traces. It is obvious that, if spreading had occurred, the values obtained with increasing distances (R) would not be a constant. The large value obtained by Valasek is most probably to be attributed to *the effect of the finite width of the microphotometric spot*, for which he has not corrected, and not to the spreading of the photographic image.

In conclusion, I wish to express my grateful thanks to Prof. Sir C. V. Raman for the suggestion of the problem, and for the kind interest he took in the investigation.

## 6. *Summary*

The angular divergence of the monochromatic X-ray reflection given by four blue-fluorescent diamonds has been measured. The diamonds were chosen to have widely different intensities of fluorescence, the intensities

being in the ratio of 1 : 4·1 : 23 : 990. The divergence of crystal reflection was measured by means of a stationary crystal, using a narrow slit as the source of X-rays, the characteristic MoK$\alpha_1$ and K$\alpha_2$ reflected beams being photographed at a large distance from the crystal. Correcting for the lack of monochromatism of the X-rays, the half-widths of the divergence for the four specimens were found to be respectively 2·7, 4·8, 13·8 and 21·4 seconds of arc, as compared with the theoretical value 2·0 for a perfect crystal, showing clearly that the more intensely blue-fluorescent a diamond is, the larger is the divergence of the reflection given by it. It is pointed out that the integrated intensity of the Bragg reflection should be proportional to the half-width of the divergence, and this has been verified to be the case for two of the diamonds studied.

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# CHEMICAL EXAMINATION OF THE RHIZOMES OF *ZINGIBER ZERUMBET*, SMITH*

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(Communicated by Dr. K. L. Moudgill, F.A.SC.)

*Zingiber zerumbet* belongs to the sub-family Zingiberacea in N. O. Sitamineæ (Sanskrit—Kumbhika-Vanasringa. Malayalam—Kattu Kolinchi). The rhizomes of this plant are used locally as a medicine for diseases of the stomach.

The rhizomes of *Zingiber officinale* (ginger), an allied member of the same family is an article of commerce and it is largely exported from this country and used as a medicine in all the pharmacopœias of the world, chiefly in the form of tinctures. Ginger has been investigated and besides the essential oil, which is an article of commerce it contains a ketone, Zingerone[1] and an alcohol, Gingerol.[2]

The rhizomes of another member of the same family, Zingiber Americans† (Lampoejang pait) was re-examined by A. G. Van Veen.[3] He studied in greater detail the sesquiterpene ketones, isolated previously by Von Romburgh.[4] He obtained " an optically inactive mixture (m.pt. 62–68° C.) which on crystallisation or distillation affords mixtures, m.pt. 67° or 69° C. respectively of isomerides, $C_{15}H_{22}O$ (I). I gives semicarbazone, $C_{16}H_{25}ON_3$ (II) m.pt. 155-160° C. and an oxime $C_{15}H_{23}ON$, m.pt. 179° C. ; both are mixtures. Hydrogenation of I (m.pt. 68°) gives a mixture of ketones $b_{1\cdot7}$ 125 – 45° C. which affords fractions (III), m.pt. 60° C. mainly $C_{15}H_{30}O$ (aliphatic) and (IV) $b_{0\cdot2}$ 125 – 33° C. mainly $C_{15}H_{28}O$ (monocyclic). III gives a semicarbazone $C_{16}H_{33}ON_3$ melting at 187° C. and an oxime $C_{15}H_3{}_1ON$, m.pt. 105° C....." But the work described below was done a little earlier than the publication of the results by A. G. Van Veen, to find out if the active principles of Zingiber Zerumbet and officianale are similar.

## *Discussion of Results*

The alcohol soluble part of the root contains a crystalline solid, an essential oil (both soluble in light petrol (50°–60° C.), a solid, gritty resin (ether soluble), a glucoside (?), glucose and potassium chloride.

* Part of a Thesis submitted for the M.Sc. Degree of the Madras University in March 1938.

† A doubt is expressed in the paper about this rhizome being the same as *Zingiber zerumbet*.

The crystalline solid (m.pt. 67–68° C.) had the molecular formula $C_{15}H_{22}O$. It distilled without decomposition *in vacuo*. A semicarbazone, a phenyl hydrazone and an oxime have been prepared. It was found to be unsaturated. The semi-carbazone of the tetrahydro product has been prepared. On oxidation with alkaline hydrogen peroxide it gave an oxide. With hydrogen sulphide in an ammoniacal alcoholic solution it gave solid sulphide.

Following the reasoning of Bradfield, Penfold and Simonson[5], it contains the group $-CH_2-CO-CH=CH-$ because "on oxidation with hydrogen peroxide in alkaline solution an oxide ..... is obtained. The latter reaction is known to be characteristic of ketones containing the ethylenic linkage in the $\alpha\beta$-position to the carbonyl group and confirmatory evidence of the presence of this group was afforded by the preparation of an unstable crystalline compound with hydrogen sulphide."

These properties of the substance show that it is a new sesquiterpene ketone.

*Experimental*

The rhizomes used in this work were specially collected locally, washed and dried in air. In a preliminary experiment a sample of the sliced, air-dried, rhizomes (20·6 gm.) was extracted in a Soxhlet apparatus with various solvents in succession.

TABLE I

| Order of extraction | Solvent | Weight of extract | Amount extracted |
|---|---|---|---|
| | | | % |
| 1 | Petrol (50–60° C.) .. .. | 0·25 | 1·25 |
| 2 | Chloroform .. .. .. | 0·55 | 2·60 |
| 3 | Ether .. .. .. | 0·85 | 4·12 |
| 4 | Alcohol .. .. .. | 0·21 | 1·00 |

The petrol extract was an oil containing a white crystalline substance, while the chloroform, ether and alcoholic extracts gave resinous masses. The rhizomes gave 23·3% of an ash containing carbonate, phosphate, sulphate, chloride, iron, magnesium and potassium.

25 lbs. of fresh air-dried rhizomes were then extracted with hot 95% alcohol in a continuous extractor. The alcohol was distilled off from the reddish extract and extracted with light petrol (50–60° C.). An aqueous layer (A) a semi-solid layer (B) and a petrol layer (C) separated. These were separately examined.

The aqueous layer (A) after boiling with animal charcoal and evaporating down deposited potassium chloride crystals. The concentrated aqueous

extract was extracted with amyl alcohol. The new aqueous layer gave with phenylhydrazine an Ozazone (m.pt. 205-06° C.) which did not depress the m.pt. of glucozozone. The amyl alcoholic extract reduced fehlings solution after hydrolysis with dilute hydrochloric acid. This suggests the presence of a glucoside.

The semi-solid (B) was resolved into ether-soluble and ether-insoluble parts. The ether soluble part was further resolved into acids and phenolic compounds. None of these gave crystalline compounds but only yellowish resinous products.

From (C) the petrol was driven off, when a thick, dark-brown, viscous oil with a white crystalline solid in suspension was obtained. The solid was separated. [($C_1$) Yield 0·5%.] The oil was steam-distilled, when a small quantity of a volatile, fragrant smelling essential oil was obtained, the bulk consisting of fixed oils. The essential oil had, density (30° C.) = ·961 and Ref. Index (30° C.) 1·5020.

The solid ($C_1$) was re-crystallised many times from dilute alcohol and finally a pure, white solid, crystallising in long needles and melting at 67–68° C. was obtained. The solid distilled unchanged at 155–157° C./5–7 mm. It solidified in the receiver and this solid melted at 68·5° C. alone and at 67·5° C. when mixed with the original.

It gave C = 82·9% H = 10·13%.

M. Wt. 203 (Lansberger).

$C_{15}H_{22}O$ requires C = 82·96%; H = 10·1%. M. Wt. 218.

When kept in a corked tube it slowly changed into a thick liquid from which the original solid could not be recovered. The change was not due to absorption of moisture.

*Properties and reactions.*—The solid was very soluble in benzene, ethyl alcohol, acetone, chloroform, carbon tetrachloride and carbon bi-sulphide. It was insoluble in hot and cold water. It could be crystallised from dilute alcohol. It did not show any rotation in chloroform solution. An alcoholic solution of the solid did not give any colour with ferric chloride. It did not react with dilute hydrochloric acid. With concentrated sulphuric acid it gave an yellow solution which changed to dark red. With concentrated nitric acid, yellow amorphous nitrated products were obtained. It did not react with acetyl chloride, nor did it contain a methoxy group as tested by a Zeizel determination. It decolourised potassium permanganate solution as well as bromine water. With bromine in chloroform, 0·2 gm. of the substance in chloroform took up 0·29 gm. of bromine and gave an yellowish oily bromide ($C_{15}H_{22}Br_2O$ requires ·28 gm.). With dry HCl gas, it gave

only a liquid product. It reacted with phenyl hydrazine, semicarbazide hydrochloride and hydroxylamine hydrochloride.

(Semicarbazone m.pt., 163° C.

Found: N, 15·7% ; $C_{16}H_{25}N_3O$ requires N, 15·3%;

Phenylhydrazone: m.pt., 144–146° C.

Found: N, 8·7%; $C_{21}H_{28}N_2$ requires 9·1%.

Oxine: m.pt., 172–173° C.).

The substance was hydrogenated in alcohol medium, using freshly precipitated platinum as catalyst, when a liquid tetra-hydro product was obtained. (0·997 gm. took up 225 c.c. of $H_2$ at N.T.P. ·997 gm. of $C_{15}H_{22}O$ requires 228 c.c. at N.T.P. for two molecules of $H_2$.) The tetrahydro product was a sweet smelling liquid distilling at 155–157° C./2–3 mm. Ref. Index (30° C.) = 1·5013. (Found : C = 81·2%, H = 11·1%. $C_{15}H_{22}O$ requires C = 81·1%, H = 11·7%.) The tetrahydro product gave a crystalline semicarbazone melting at 193° C. (Found: N = 15·5%. $C_{16}H_{29}N_3O$ requires N — 15·1%.)

On reducing the substance with sodium and alcohol a pleasant smelling liquid, distilling at 175–182° C./10 mm. was obtained. It failed to give crystalline acetyl and *p*-nitro benzoyl derivatives.

An ice-cold solution of the substance in methanol was oxidised with hydrogen peroxide, when an oxide, re-crystallisable from light petrol and melting at 50–60° C. was obtained. (Found: C, 76·2%; H, 9·9%; $C_{15}H_{22}O_2$ requires C, 76·9%; H, 9·4%.)

With hydrogen sulphide, an alcoholic solution of the substance, made alkaline with liquor ammonia, gave a light yellow solid which separated after 12 hours at − 8° C. This sulphide melted between 105° and 115° C.

The author thanks Dr. K. L. Moudgill for guiding this work and Dr. P. P. Pillai for many helpful suggestions.

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# MAGNETIC PROPERTIES OF AUGITE

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

## *1. Introduction*

Augite is a monoclinic crystal belonging to the pyroxene group of minerals. It is a meta-silicate of calcium, magnesium and aluminium; and iron is present in it in the ferrous and ferric states. The analyses of different specimens reported (Iddings) show that its chemical composition is variable and the amount of iron oxides it contains is comparatively small, from about 6% to a maximum of 17%. Four crystals of augite were chosen from the crystallographic collection of Sir C. V. Raman and magnetic studies were made on them with the object of getting information regarding the behaviour of this mineral.

The crystals were short and thick prisms with masses lying between 153 mgm. and 233 mgm. They were black and opaque and bounded by the (100), (010), (110) and ($\bar{1}$11) faces which were very well developed, smooth and lustrous. Excepting crystal No. 1 they were twinned on the (100) plane. The angles between the (110) and (100) faces and the (110) and (010) faces of crystal No. 1 were measured approximately with a goniometer and found to be 136°–20′ and 133°–40′ respectively, in approximate agreement with the values 136°–27′ and 133°–33′ respectively quoted by Dana for the same angles.

## *2. Experiments and Results*

The magnetic axes of the crystals were determined by suspending them suitably in a uniform magnetic field and observing their orientation. Since by a preliminary examination the crystals were found to exhibit remanent magnetisation, they were demagnetised each time before suspending them in the field. Crystal No. 1 which was untwinned had the crystal axis *b* as one of the magnetic axes and the axis of maximum susceptibility in the *b* plane was at an angle of 48½° to the C axis. For the remaining three crystals which were twinned in the (100) plane the axis *b* was one of the magnetic axes but there were differences in the directions of the other two magnetic axes, presumably due to the twinning. In crystal No. 2 the axis of maximum

susceptibility in the *b* plane was at an angle 85½° to the C axis, *i.e.*, nearly normal to it, whereas in crystal No. 3 it was parallel to the C axis. In crystal No. 4 these two magnetic axes were not definite and the orientation of the crystal when suspended with the *b* plane horizontal changed as the field strength increased tending to place the C axis along the field. The crystal was longest along the C axis and the change of orientation was possibly due to the low magnetic anisotropy in the *b* plane (observed from later measurements) and its asymmetry of shape.

The intensity of magnetisation acquired by the crystals even in strong magnetic fields was small and could not be measured by the induction method. Hence the susceptibility of the crystals was measured by the Curie-balance for a wide range of field strength. The crystals were suspended rigidly with the magnetic axes, lying approximately in the direction of the field. For crystal No. 4 which showed the variation of orientation of the *b* plane with field strength, the susceptibilities along the C axis and perpendicular to it in the *b* plane were measured. About a dozen observations were made for different field strengths ranging from 340 oers to 5800 oers. The variation of the susceptibility of crystal No. 2 along the *b* axis is given in Table I. A similar variation was obtained in all the other cases; the susceptibility decreased as the field strength increased, rapidly at low fields and slowly at higher fields. The results for the lowest and the highest fields employed are given in Table II for all the specimens.

The remanent magnetic moment of the crystals along the three magnetic axes were roughly estimated. The crystal was demagnetised thoroughly and a thin glass rod 1″ long and less than ½ mm. thick was fixed to it by shellac perpendicular to one of the magnetic axes. It was attached by this glass rod to the end of a fine quartz fibre of known torsional constant and its period of oscillation in the earth's magnetic field determined. The crystal was detached from the fibre and held fixed to a support by the glass

TABLE I

*Variation of the mass susceptibility* χ *of crystal* 2 *along the* b *axis*

| Field strength (oers.) | 340 | 620 | 910 | 1200 | 1500 | 1800 |
|---|---|---|---|---|---|---|
| $\kappa \times 10^6$ | 448 | 365 | 332 | 293 | 268 | 252 |
| Field strength (oers.) | 2300 | 2900 | 4200 | 5000 | 5800 | |
| $\kappa \times 10^6$ | 211 | 181 | 140 | 122 | 112 | |

TABLE II

*Mass susceptibility of crystals* 1 *to* 4 *along the three magnetic axes*

| Crystal No. | $\varkappa \times 10^6$ | | | Field strength (oers.) |
|---|---|---|---|---|
| | Axis of max. susc. in the *b* plane | Axis of min. susc. in the *b* plane | *b* axis | |
| 1 | 430<br>185 | 420<br>181 | 330<br>164 | 1100<br>3600 |
| 2 | 680<br>119 | 650<br>114 | 450<br>112 | 340<br>5800 |
| 3 | 970<br>151 | 890<br>154 | 690<br>148 | 340<br>5800 |
| 4 | 630<br>126 | 620<br>125 | 570<br>125 | 340<br>5800 |

rod, between the pole-pieces, and magnetised in the direction of one of the magnetic axes by a strong field of about 15,000 oers. The crystal was transferred to the fibre, the direction of its magnetisation made to coincide with the earth's field when the crystal was at rest and its period of oscillation determined. An appreciable decrease in the period was observed from the previous value in all the cases, 10·1 sec. and 4·4 sec. being the values in the demagnetised and magnetised states respectively in one particular case. The remanent magnetic moment per gm. of the crystal was calculated from the observations; and the results are tabulated below.

TABLE III

*Remanent magnetic moment per gm.*

| Crystal No. | Aixs of max. susc. in the *b* plane | Axis of min. susc. in the *b* plane | *b* axis |
|---|---|---|---|
| 1 | 0·067 | 0·069 | 0·027 |
| 2 | 0·042 | 0·039 | 0·018 |
| 3 | 0·019 | 0·016 | 0·011 |

An estimate of the coercive force was also made in the following manner. The crystal was suspended by a single strand of silk fibre in a uniform magnetic field and the field was increased to a high value of about 15,000 oers. The current in the magnet was slowly reduced to a low value, then switched

off and reversed by the commutator in the circuit. If the current was sufficiently low, it was found that the crystal rotated and came to rest in the opposite direction, showing that the field applied in the opposite direction had not completely destroyed the remanent magnetisation and that owing to the residual component of magnetisation the crystal reversed its direction of orientation. But if the current sent in the opposite direction was high the crystal did not reverse its direction, showing that the remanent magnetisation had at least been completely destroyed. These two fields applied opposite to the direction of magnetisation, one for which the crystal reversed its direction and the other for which it did not reverse its direction, were obtained by trial to be as close to each other as possible, and their mean value was taken as a rough measure of the coercive force. The two values usually differed by 50 oers. The coercive force was thus estimated to be 1030 oers and 650 oers for the axes of maximum and minimum susceptibility respectively in the *b* plane of crystal No. 2, 320 oers and 820 oers in the *b* plane of crystal No. 3 and 440 oers for the C axis of crystal No. 4. The coercive force along the *b* axis could not be found by this method for its orientation was always normal to the field, it being the axis of lowest susceptibility.

### *Discussion*

The definite orientation of the crystals in a uniform magnetic field show that they possess definite magnetic axes. In crystal No. 1 which is not twinned the magnetic axes are consistent with its monoclinic symmetry. In the other crystals the *b* axis is one magnetic axis as required by the crystal symmetry and the twinning has altered the directions of the other two magnetic axes in the *b* plane.

The value of the susceptibility and its variation with field strength is characteristic of ferromagnetic materials with very low intensity of magnetisation. As the field strength increases there is a rapid fall of the susceptibility at low fields followed by a slow decrease at high fields. At fields as high as 5800 oers there is appreciable decrease of the susceptibility with increase of field strength, showing that saturation is not reached at these field strengths. The magnetic anisotropy is very pronounced at low fields and the crystals tend to be magnetically isotropic at high fields. For all crystals the susceptibility along the *b* axis is less than that along the other two axes.

The values of the remanent magnetisation and coercive force as determined are only rough estimates of the quantities. For all the crystals the remanent magnetisation in the two directions of the *b* plane are nearly equal, but that along the *b* axis is smaller. The very high values of the coercive force are also notable.

The ferromagnetism of augite is very striking in view of the fact that its iron content is small, the amount of iron oxides being usually about 10%. The magnetic characteristics of small traces of iron present as an impurity are very complex; but in augite it is not probable that iron is present as an impurity, for the crystals show definite magnetic axes as required by crystal symmetry and the directions of the magnetic axes are also altered by twinning.

The sincere gratitude of the author is due to Professor Sir C. V. Raman for suggesting the problem, for the loan of the crystals for study and for his keen interest and guidance in this work.

## 4. *Summary*

The magnetic properties of four crystals of augite, three of them twinned in the (100) plane were studied. The crystals were axially ferromagnetic, with low intensity of magnetisation. Saturation was not reached at fields as high as 5800 oers. They were anisotropic magnetically at low fields and tended to become isotropic at high fields. The coercive force was found to be very large in all the cases.

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# WAX AND RESIN COMPONENTS OF *LEPTADENIA RETICULATA*

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A number of medicinal plants belonging to the family Asclepiadaceæ have been recently examined and found to contain resinols. *Asclepias syriaca* seems to have been the earliest to be studied. The milky sap of this plant was examined at various times by Marek[1] who noticed the presence of butyric acid esters of various alcohols whose identity was indefinite. The colour reactions of these substances as noted by him were not entirely in agreement with those possessed by sterols. At a later stage he was able to isolate from this mixture of esters a compound melting at 240–41° and having the formula $C_{30}H_{49}OCOCH_3$. Van Romburgh identified this as β-amyrin acetate. It was therefore possible that resinols existed in the sap. Working with the same plant Schmid *et al.*,[2] definitely showed that the main bulk of the material did not possess the prominent characteristics of sterols, *e.g.*, precipitation with digitonin, and that the alcohols consisted of a mixture of α- and β-amyrins.

A similar result was obtained by Matzuret[3] in regard to the composition of *Asclepias carnuti*. It contained esters of aliphatic acids with complex alcohols among which could be identified α- and β-amyrins. Earl and Doherty[4] in a paper on *Sarcostemma australe* which also belongs to this family, recorded the analysis of the wax obtained by extraction with ether. Though direct crystallisation of the unsaponifiable matter was not satisfactory, acetylation and subsequent fractionation enabled the isolation of α- and β-amyrins to be made.

*Hemidesmus indicus*, also known as Indian Sarasaparilla, was investigated by Dutta *et al.*,[5] who stated that it contained besides the 4-methyl ether of β-resorcylic aldehyde, two sterols, hemidesterol and hemidesmol. This root along with that of *Decalepis Hamiltonii* both of which belong to the family Asclepiadaceæ was carefully investigated by Murti and Seshadri.[6] These are closely allied plants and possess similar components. The unsaponifiable part of the waxy matter consisted mainly of resinols and only minor quantities of sterols seemed to be present. The resinol portion

contained α- and β-amyrins primarily with lupeol as a minor component in the case of *Decalepis Hamiltonii* whereas with *Hemidesmus indicus* the reverse was the case. They seem to occur as esters of steam volatile lower fatty acids and also of fatty acids of higher chain-lengths. β-Amyrin acetate could be isolated from the mixture of esters. In this connection it may be mentioned that lupeol was known to occur in the plants belonging to the families Sapotaceæ, Rutaceæ and Leguminoseæ[7]; from the above results it is established that some members of Asclepiadaceæ also contain lupeol.

Another well-known plant of this family is *Calotropis gigantea.* The root bark was first investigated by Hill and Sirkar[8] who employed its alcoholic extract. They reported that besides gutta-percha like material two alcoholic substances, mudarol and akundarol existed as esters with isovaleric acid and they believed that these substances were definitely different from resin alcohols characterised by Cohen, Van Romburgh and others. More recently Basu and Nath[9] carried out a study of the milky juice of *Calotropis gigantea* and reported the isolation of a new sterol which they named calosterol. Its properties were abnormal for a sterol and in general resembled those of resinols. The study of the various parts of *Calotropis gigantea* that has been carried out by us[10] has definitely established the existence of resinols in this plant also.

Another species of Calotropis is *Calotropis procera.* A recent study of the latex of the plant has been made by Hesse *et al.*[11] They have recorded that α-lactucerol is the sole alcoholic component and that it exists as acetate and isovalerate. It is capable of isomeric change into isolactucerol. Though there has been considerable variation in the description of α-lactucerol, it is considered to be a triterpene alcohol.

*Leptadenia reticulata* is another plant of this family commonly available in the hilly tracts of the East Coast of India. It is a tender creeper and seems to find an occasional use in nose and ear troubles. With a view to make sure if all the members belonging to Asclepiadaceæ invariably contain resinols, a composite sample of this creeper consisting of stems and roots has now been examined. Since in all the cases that have been studied so far resinols come in the ligroin soluble fraction, only this solvent has now been used for extraction. The ligroin extract yields about 1·5% of waxy matter which has been separated into fractions and studied in detail. As the result it has been found that the major portion of the wax consists of aliphatic components which are esters of long-chain alcohols, $C_{28}$–$C_{34}$ with long-chain acids, $C_{28}$–$C_{32}$. A very small quantity of a substance melting at 115° was also obtained. It could not be completely characterised.

Further, the extract contains about 12·0% of sterols and it is remarkable that these are found to occur entirely free and not in the form of esters. For purposes of separating the individual sterols, bromo-derivatives of their acetates were prepared and fractionated according to the method of Windaus and Hauth.[12] The top fraction, forming about 75% of the mixed bromo-compounds, melted round about the temperature recorded in the literature for the tetra-bromide of stigmasteryl acetate, and the crystal structure also agreed. Further the acetate and the sterol obtained from the bromo-compound on de-bromination and subsequent hydrolysis, possess properties agreeing closely with those of stigmasteryl acetate and stigmasterol; consequently this fraction is considered to consist of stigmasterol. The more soluble bromoacetates, the minor fraction, on de-bromination and repeated purification, yielded an acetate which closely resembled that of γ-sitosterol. The properties of the free sterol obtained from it are also in close agreement with those of the above-mentioned sterol. Hence, this fraction is considered to contain γ-sitosterol. It is therefore concluded that the sterol mixture consists of stigmasterol as the major component (75%) and γ-sitosterol (25%) as the minor component. No resinol could be found. It is not definite if this could be correlated with the fact that the plant does not yield a milky latex. However, the conclusion may be drawn that though most plants of the family Asclepiadaceæ contain resinols there are others devoid of them.

*Experimental*

The whole plant excepting the leaves was employed for the investigation. A composite sample of the stems and roots was shredded into small bits, dried in the sun and then ground into coarse powder. About 4 kilograms were extracted in kilogram lots with ligroin for about 20 hours. Most of the solvent was removed by distillation and the resulting residue was heated on a water-bath to remove the last traces of the solvent. The dry extract (42·0 g.) thus obtained appeared as a dark green semi-solid. It was extracted 5 times using each time 200 c.c. of boiling alcohol; the clear solutions were decanted hot and mixed together. The undissolved residue was marked (A) (5·0 g.). The combined alcoholic solution when kept for a day deposited a bulky solid melting between 60–85°. This was separated and marked (B). When the mother-liquor was concentrated to about 200 c.c. a soft crystalline looking solid contaminated with resin was obtained. A little more produced by further concentrations to 50 c.c. was also added. This fraction was marked (C) (7·0 g.). When tested by means of the Salkowski and Liebermann-Burchard reagents fractions (A) and (B) produced no colour indicating that they were free from resinols and sterols and fraction (C) gave the tests characteristic of sterols.

Fraction (A) was rather sticky and repeated purification did not yield a definite solid; even after saponification the products could not be satisfactorily purified.

*Fraction B* (*aliphatic wax esters*).—This fraction (27·0 g.) was obtained as a green solid with very indefinite melting point. In order to separate it into fractions it was digested with boiling acetone (1000 c.c.). A small portion was insoluble; additions of ether (400 c.c.) did not make any difference. The insoluble solid was filtered off and marked $B_1$. Concentration of the filtrate to 300 c.c. resulted in the separation of a pale green solid melting at about 87°. After digestion with boiling ethyl acetate and crystallisation successively with benzene-alcohol mixture and chloroform a colourless solid melting at 90–92° was obtained (6·0 g.). This was marked $B_2$. By working up the acetone and ethyl acetate mother liquors and purifying the product another fraction ($B_3$) melting at 86–89° was collected.

$B_1$ was sparingly soluble in ordinary solvents; it was purified by boiling with a mixture of benzene and chloroform when it melted at about 110°. It was finally crystallised from a mixture of chloroform and acetic anhydride and was obtained as colourless rhombs which melted at 115°. It gave negative Salkowski and Liebermann-Burchard reactions (Found: C, 80·1; H, 11·7%; $C_{32}H_{20}O$ requires C, 80·0; H, 11·1%.). The results of analysis agree with the above empirical formula. The final yield was very small and no further data could be obtained due to dearth of material.

$B_2$ had an acid value of 6·9 and seemed to consist mostly of wax esters (Found: C, 82·5; H, 13·4; $C_{62}H_{124}O_2$ requires C, 82·7; H, 13·8%.). It (5·0 g.) was subjected to saponification by boiling its benzene solution (300 c.c.) with 8% alcoholic potash (300 c.c.) for 20 hours. Subsequently an alcoholic solution of calcium chloride (30·0 g. in 400 c.c.) was added and the boiling continued for 2 more hours. After concentrating the mixture, the resulting solid was filtered hot and washed with small amounts of alcohol. It was then repeatedly extracted with boiling acetone (200 c.c.) to remove the unsaponifiable matter from the soap. On keeping the acetone solution for a day a colourless solid separated out and it was purified by recrystallisation from chloroform. The first crop (I) (2·1 g.) melted at 92° and the melt set to a solid at 91°. The subsequent crop (II) was negligible in amount and melted at 88–90°. Solid (I) was subjected to acetylation by boiling with acetic anhydride and sodium acetate. The resulting product was found to be an acetate and after crystallisation from ether-alcohol mixture it melted at 76° (Found: C, 80·2; H, 13·3; $C_{36}H_{72}O_2$ requires C, 80·6; H, 13·4%.). The melting point of the acetate corresponds to an

alcohol mixture of average chain length $C_{34}$ and the melting point of the alcohol mixture also supports the conclusion that this fraction consisted of $C_{34}$ alcohol and near homologues.

The calcium soap left after extraction of the unsaponifiable matter was decomposed by boiling with acetic acid (300 c.c.) and the mixture was largely diluted with water. The resulting solid was again digested with boiling acetic acid and the free acids thus obtained were purified by dissolving in acetone-chloroform mixture. On keeping the solution for a day a colourless crystalline solid (2·5 g.) melting at 90–92° was obtained. Its melting point could not be raised by further crystallisation (Found: C, 79·8; H, 13·3; $C_{30}H_{60}O_2$ requires C, 79·7; H, 13·3% and $C_{32}H_{64}O_2$ requires C, 80·0; H, 13·3%.). It had a molecular weight of 467·8. Consequently it had a mean chain length of $C_{31}$ and probably consisted of $C_{30}$ and $C_{32}$ acids.

Fraction ($B_2$) thus seemed to be mostly made up of esters of alcohol of $C_{31}$ dimension and its near homologues with acids having chain lengths of $C_{30}$ and $C_{32}$.

Fraction $B_3$ (15·0 g.) was subjected to saponification by boiling its benzene solution (500 c.c.) with an equal volume of 8% alcoholic potash for 20 hours. After removing the major bulk of the solvents, the resulting products were dried into a friable mass. The dry material was extracted in a Soxhlet with petroleum ether and acetone in succession to remove the unsaponifiable matter from the soap. To ensure complete saponification the unsaponifiable matter obtained after removal of the above solvents was again subjected to saponification by boiling its benzene solution (150 c.c.) with sodium ethoxide (3·5 g. of sodium in 200 c.c. of alcohol) for 4 hours. Then an alcoholic solution of calcium chloride (20·0 g. in 200 c.c. of alcohol) was added and the boiling continued for two more hours. The contents were filtered hot. The solution was concentrated to half its bulk, largely diluted with water and the resulting precipitate consisting of the calcium soaps (negligible) and the unsaponifiable matter was filtered. The precipitate was dried and was extracted with boiling acetone (500 c.c.) using 100 c.c. at a time. The acetone extracts were all mixed together and on concentrating the combined solution to about 150 c.c. a pale yellow solid (7·0 g.) separated out. It was dissolved in chloroform and filtered. After keeping for a day the chloroform solution deposited a colourless solid (4·0 g.) melting at 89–90° and setting at 88·5°. It appeared as rhombs under the microscope (Found: C, 82·8; H, 13·8; $C_{32}H_{66}O$ requires C, 82·4; H, 14·2%). On acetylation by boiling with acetic anhydride and sodium acetate it yielded

an acetate melting at 73·0°. The melting point of the acetate corresponds to an average chain length of 32 C atoms in the alcohol. The chloroform mother liquor yielded a solid which formed an acetate melting at 70–71° indicating that it consisted of lower homologues. In the first saponification itself, the esters were almost completely decomposed. Consequently, the major bulk of the acids derived from them were obtained as their potassium salts and were liberated by heating the potassium soap with dilute sulphuric acid. The acids (7·5 g.) thus obtained were highly coloured and most of the colour was removed by treating their benzene solution with 'norit'. The solvent was completely removed by distillation and the residue was repeatedly crystallised from acetone and chloroform in succession. The top fraction (3·9 g.) melted at 89–91° and had a molecular weight of 460·4; consequently it may be considered to have a mean chain length of $C_{30\cdot6}$ and probably consisted of $C_{30}$ acid and its higher homologues. The second fraction (2·1 g.) melted at about 88° and had a molecular weight, 422·8. It had a mean chain length of $C_{29\cdot3}$ and the fraction was considered to be a mixture of $C_{30}$ acid and its lower homologues.

Fraction ($B_3$) was therefore considered to be a mixture of esters of long chain alcohols, $C_{28}$–$C_{32}$, with acids of similar chain lengths.

*Fraction* (*C*) (*stigmasterol and γ-sitosterol*).—The crude fraction (7·0 g.), on crystallisation from acetone, yielded a colourless solid in the form of tiny plates melting at 132–34°. With the Salkowski reagent it gave a blood red colour in the chloroform layer while exhibiting green fluorescence in the acid layer; with the Liebermann-Burchard reagent a play of colours—pink-blue-green was produced. It formed a precipitate with digitonin in alcoholic solution. In order to test for the presence of esters the crystalline solid was subjected to saponification by boiling with alcoholic potash. The solvent was distilled off as far as possible and the concentrate was diluted with water and ether extracted. After removing the ether, the residue was fractionally crystallised from alcohol and three crystalline fractions were collected. All of them appeared as broad plates and melted at 134-36°. $(\alpha)_D$, $-40\cdot2°$ in chloroform. However, they did not show any depression in their melting points when mixed with the original solid. The aqueous alkali solution obtained after ether extraction, when rendered acidic, did not give either steam-volatile or non-volatile acid.

*Acetylation*.—The above fractions were mixed together and the combined solid (4·0 g.) was subjected to acetylation by boiling with acetic anhydride (25 c.c.) and sodium acetate (5·0 g.) for 3 hours. The resulting product, after crystallisation from ether-alcohol mixture, was obtained as

broad colourless plates melting at 130–32°. No improvement in the melting point could be effected by further crystallisation from various solvents. $(\alpha)_D$, $-48{\cdot}7°$ in chloroform.

*Bromo-acetates.*—The crystalline acetate (3·0 g.) was dissolved in ether (150 c.c.) and excess of bromine dissolved in glacial acetic acid was added in drops, all the while keeping the ether solution at 0° C. After allowing it to stand for 12 hours in ice, a colourless crystalline bromo-derivative (2·2 g.) had separated out and it melted at 199° (decomp.). On crystallisation from glacial acetic acid and then from chloroform-alcohol mixture, it was obtained in the form of well-defined rhombic plates melting at 205° (decomp.). It was considered to be the tetra-bromide of stigmasteryl acetate. The ether solution, obtained from the crude bromo-compound, on concentration to about 15 c.c. deposited a smaller amount of a crystalline product melting at about 155°.

*Stigmasteryl acetate.*—The pure bromo-acetate (1·5 g.) was debrominated by carefully boiling with glacial acetic acid and zinc dust. The resulting product, after crystallisation from alcohol, was obtained in the form of broad rectangular plates melting at 143°. $(\alpha)_D$, $-51{\cdot}7°$ in chloroform.

*Stigmasterol.*—The pure acetate (1·0 g.) was hydrolysed by boiling with alcoholic potash and the resulting sterol was recovered by ether extraction. It crystallised from alcohol in the form of broad rectangular plates and melted at 168° (Found: C, 80·6; H, 12·0; $C_{29}H_{48}O$, $H_2O$ requires C, 80·9; H, 11·6%.). $(\alpha)_D$, $-49{\cdot}2°$ in chloroform.

*γ-Sitosterol.*—The more soluble bromo-acetate fraction (0·5 g.), m.p. about 155°, was crystallised from acetic acid and the top fractions melting at about 179° were rejected. From the mother liquor, a small amount of a crystalline solid melting at about 135° was collected and purified by crystallisation from ether-alcohol mixture. It was debrominated and the resulting acetate was repeatedly crystallised from alcohol. Finally it was obtained in the form of broad plates melting at 140°. After saponification, it yielded a sterol which crystallised from alcohol as plates and melted at 142°. $(\alpha)_D$, $-41{\cdot}2°$ in chloroform. From the above data, this sterol was considered to be γ-sitosterol. It is possible that the more soluble bromo-compounds were a mixture of the derivatives of sitosterols.

From the results recorded above, fraction (C) should be considered to consist almost completely of free sterols. Stigmasterol was found to be the major component of the sterol mixture, and γ-sitosterol probably along with small quantities of other sitosterols formed the rest.

*Summary*

Past work on the chemical components of a number of plants of the family Asclepiadaceæ is reviewed. They are found to contain resinols though many of these were originally mistaken for sterols. With a view to test if this is an invariable rule another member, *Leptadenia reticulata*, has now been studied. The major portion of the wax consists of aliphatic wax esters derived from long-chain alcohols ($C_{28}$–$C_{34}$) and long-chain acids ($C_{28}$-$C_{32}$). Considerable amount of sterols occur free and the mixture seems to consist mostly of stigmasterol along with smaller amounts of sitosterols of which $\gamma$-sitosteral could be characterised. No resinols could be detected.

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# SYNTHESIS OF 5 : 6-DIHYDROXYFLAVONOLS—PART I

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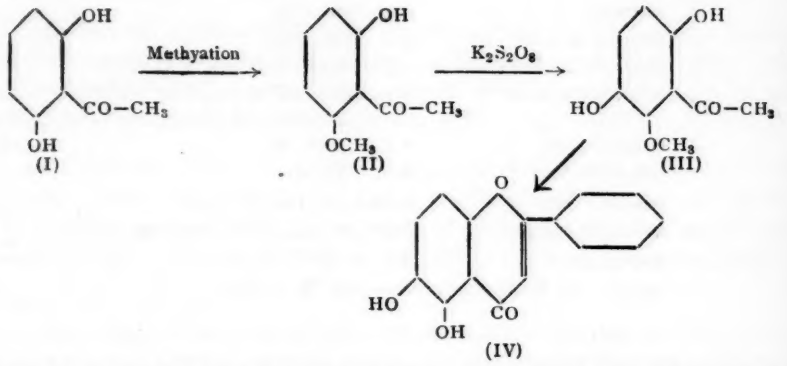
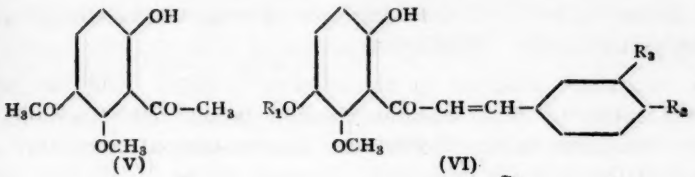
5 : 6-Dihydroxyflavonols have not so far been synthesised. In connection with the constitution of patuletin it is now found necessary to prepare them and study their properties and reactions. 5 : 6-Dihydroxy-flavone (IV) was made by Baker[1] in the course of his study of primetin; starting from 2 : 6-dihydroxy-acetophenone (I) the various stages of his synthesis are represented below:




Since the ω-methoxy derivative of (III) is not available the method of Allan and Robinson cannot be used for the synthesis of the flavonols. Consequently the original procedure of Kostanecki has been adopted. This paper records the condensation of ketone (III) with vanillin and of 5 : 6-dimethoxy-2-hydroxy-acetophenone (V) with veratric aldehyde and anisaldehyde to obtain the corresponding chalkones (VI). The conditions for getting the best yields were worked out initially using resacetophenone and its 4-methyl ether. Addition of an excess of the aldehyde component, and the use of strong aqueous alcoholic potash were found to be advantageous. It was noted that in all the cases reported here, some quantity of the flavanones (VII) accompanied the corresponding chalkones.

The conversion of the chalkones (VI) to the flavanones (VII) was carried out by means of aqueous alcoholic sulphuric acid. Even here the products




$R_1$=H or $CH_3$ $R_2$=OH or $OCH_3$ $R_3$=H or $OCH_3$

were mixtures, a portion of the original chalkones remaining unchanged. 5:6:3′:4′-Tetramethoxy-flavanone was first obtained by methylating 5:3′-dimethoxy-6:4′-dihydroxy-flavanone using methyl iodide and potassium carbonate in acetone medium. The identity of the compound was established by synthesis directly from (V) and veratric aldehyde. This is rather remarkable since in other cases of flavanones like naringin and hesperidin the methylation of the hydroxyl groups is accompanied by the opening of the flavanone ring and final methylation of the hydroxyl thus set free. The factors that contribute to this difference are not quite clear.

The chalkones described in this paper are bright red in colour whereas the flavanones are colourless. Only the former yield colour with ferric chloride whereas the latter alone give red colour when reduced with magnesium and hydrochloric acid, the colour being definitely weaker with the fully methylated flavanones. In general the chalkones are markedly less soluble.

The synthesis of the flavonols from the flavanones and their study will be reported later.

## *Experimental*

2:5:4′-*Trihydroxy*-6:3′-*dimethoxy chalkone.* (*VI.* $R_1 = H$, $R_2 = OH$, $R_3 = OCH_3$).—2:5-Dihydroxy-6-methoxy acetophenone[1] (4·0 g.) and vanillin (8·0 g.) were dissolved in alcohol (40 c.c.). To this solution aqueous potassium hydroxide (75 g. in 100 c.c. water) was added with stirring and the mixture refluxed on a water-bath for about 15 minutes. While still hot, the flask was corked tight and allowed to stand for about 24 hours. The reddish-brown liquid was then diluted to about 200 c.c. with water and acidified with hydrochloric acid with cooling under the tap, when an orange-red precipitate separated out. On crystallising it twice from alchol deep-red

considerable amount of anisic acid was produced and the yield of chalkone was reduced. The mixture was then diluted with water (100 c.c.), extracted thrice with ether to remove any anisaldehyde left unreacted and acidified with hydrochloric acid. A dark red crystalline precipitate separated out. It was filtered and macerated with sodium-bicarbonate solution to remove any anisic acid that might have formed during the process of condensation. The red coloured product was filtered, washed with water and crystallised from alcohol. A bright red substance (long needles and rectangular plates tapering at the ends) melting at 102–103° C. was obtained. Yield: 1·3 g. With ferric chloride, the chalkone produced a deep-brown colour in alcoholic solution. (Found: C, 69·2; H, 5·9; $C_{18}H_{18}O_5$ requires C, 68·8; and H, 5·7%.) The yield of the flavanone recovered from the mother liquors was very small (about 0·1 g.).

5:6:4'-*Trimethoxy flavanone.* (*VII.* $R_1 = CH_3$, $R_2 = OCH_3$, *and* $R_3 = H$).—This compound was obtained from the foregoing chalkone. The unchanged chalkone was separated with the help of a very dilute solution of sodium hydroxide. The flavanone (0·5 g. from 1 g. of the chalkone) crystallised from alcohol in the form of colourless large rectangular plates melting at 154–155° C. It gave no colour with ferric chloride in alcoholic solution. On reduction with magnesium and hydrochloric acid only a weak red colour was obtained in alcoholic solution. (Found: C, 69·3; H, 6·0; $C_{18}H_{18}O_5$ requires C, 68·8; and H, 5·7%.)

*Summary*

Methyl ethers of 5:6-dihydroxy-chalkones and flavanones have been prepared. 2:5-Dihydroxy-6-methoxy acetophenone has been condensed with vanillin and 5:6-dimethoxy-2-hydroxy-acetophenone with veratric aldehyde and anisaldehyde; the resulting chalkones have been converted into the flavanones. In the above reactions mixtures of chalkones and flavanones result.

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# CHEMICAL EXAMINATION OF THE FLOWERS OF *PONGAMIA GLABRA* AND A NOTE ON THE GLYCOSIDIC COMPONENTS OF *BUTEA FRONDOSA* FLOWERS

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IN the past the seeds and the roots of *Pongamia glabra* have been studied in detail. The former contains a fixed oil, some waxy matter consisting mostly of-long chain fatty acids and three crystalline substances, karanjin, pongamol and glabrin. Karanjin has been investigated in detail, its constitution established and synthesis effected. The other two are still under study.[1] The root bark yields a new crystalline substance named kanugin whose constitution is again unsettled.[2] The flowers of this plant have also been recorded to be of medicinal value. An attempt has now been made to make a complete analysis of this plant material, to isolate crystalline substances, and identify or characterise the components.

The flowers of *Pongamia glabra* are small in size and they fall down in large quantities in the months of January and February. This is the main season and there is another flowering later on when smaller quantities could be obtained. When fresh, the colour is ivory white and it turns yellowish brown on drying. In a preliminary examination a small quantity of the dry flowers was extracted successively in a Soxhlet extractor with different solvents and each extract studied. For a large-scale examination ligroin, ether and alcohol alone were used. The ligroin extract was separated into several fractions using alcohol. The main component was wax which was found to contain about 12% of hydrocarbons and the remainder was made up of esters derived from alcohols of $C_{24}$ to $C_{34}$ dimensions and fatty acids with chain lengths $C_{24}$ to $C_{30}$. A small amount of oil resembling in its characteristics the fixed oil from the seeds was also present. Besides these a small quantity of a colourless crystalline substance melting at 212° was isolated from the ligroin fraction. It does not give the reactions for sterols or resinols, but seems to resemble in a way karanjin and the other crystalline principles isolated from the seeds and roots. It is only feebly bitter and feebly toxic to fish. Its composition may be represented by the formula $C_{15}H_{12}O_5$; it is named ' pongamin '.

The ether extract of the ligroin extracted residue was a coloured solid from which could be isolated two crystalline substances. The first

was a yellow substance which answered all tests for kæmpferol; it occurred free. The second was a colourless solid obtained after saponifying waxy matter and was identified as γ-sitosterol.

The final extraction with alcohol was made in two stages, first using alcohol of about 90% strength and subsequently 80% alcohol. This procedure was already employed in connection with the roots of *Decalepis Hamiltonii*.[3] From the extract a sparingly soluble fraction crystallised out. This could be again separated into two parts using their solubility in water. The water insoluble part was found to be a phytosterolin agreeing in all its properties with γ-sitosterol monoglucoside. The same substance was also isolated from the flowers of *Butea frondosa*, another leguminous plant. The water-soluble portion was a sweet-tasting nitrogenous substance closely resembling glabrin[1] in most of its properties. It however differs in having a different composition and in having a lower rotation. It is therefore named neoglabrin.

The more soluble portion of the alcohol extract contained a saponin which is named glabrosaponin. It seems to have the composition $C_{50}H_{84}O_{23}$ and the aglucone seems to have the formula $C_{30}H_{50}O_5$. The sugar portion is rather complex and yields an indefinitely melting osazone mixture. A number of triterpene saponins isolated from plants, are known to contain three or four different sugar groups in their molecules. But their constitutions are still uncertain. It may be recalled here that a similar though not identical saponin was found to be present in the flowers of *Butea frondosa*.

Of the different parts of the tree so far examined the flowers provide the largest number of extractable components. Besides wax and oil, they contain pongamin, kæmpferol, neoglabrin, phytosterolin and glabrosaponin; the last two are not found even in the seeds. Waxy matter is present in the maximum amount in the flowers. Kæmpferol has already been found in plants of the family Leguminoseæ (senna, indigo, etc.) and hence its occurrence in the flowers of the pongamia is not unusual; but it is remarkable that it occurs entirely free and not as glycoside.

There exists a general resemblance between the components of these flowers and of the flowers of *Butea frondosa* though in details differences exist. Besides colouring matter they both contain resinol-glycosides (saponins), sterolin (the same substance, γ-sitosterol glucoside) and wax. The colouring matter is different, in one case kæmpferol is a flavonol and in the other case it is butin, belonging to the flavanone group, and its derivatives. Pongamia wax contains some hydrocarbons whereas the Butea flower wax is composed almost completely of esters.[4]

### *Experimental*

The fresh flowers were collected in the month of February from the trees of the Andhra University forest area in Waltair, dried quickly in the sun and preserved in covered tins for subsequent use. They were ground into a coarse powder and employed in the following experiments.

100 grams of the dry material were extracted in a Soxhlet extractor successively with several solvents. The yields and the general characteristics of the various extracts are given below.

| Solvent | Yield % | Nature of the Extract |
|---|---|---|
| 1. Ligroin .. .. .. | 0·9 | Pale brown semi-solid consisting of waxy and oily matter |
| 2. Ether .. .. .. | 0·5 | Dark green semi-solid ; contained a yellow crystalline substance having properties of hydroxy-flavones |
| 3. Acetone .. .. .. | 0·2 | Yellow waxy matter |
| 4. Ethyl alcohol .. .. | 1·0 | An almost colourless solid partly soluble in water |

As already mentioned in the Introduction, when working with large quantities for purposes of detailed study, only ligroin, ether and alcohol were used as solvents and acetone was omitted since it did not extract much of any distinctive material.

*Ligroin Extract*

The dry flower powder (10·0 *kg.*) was extracted with ligroin (b.p. 80–110°) in a continuous extractor in batches, each batch being extracted for 20 hours. The major bulk of the solvents was then recovered by ordinary distillation and the last traces were removed under reduced pressure. The residue (90·0 g.) thus obtained was semi-solid in consistency and light brown in colour and had a faint aromatic odour. It was digested under reflux with boiling alcohol (500 c.c.) for 15 minutes, the supernatant solution was poured off and the residual heavy liquid again extracted four times in a similar manner. The insoluble portion gradually solidified on cooling and was marked (A) (40·0 g.). The collected alcoholic solution was concentrated to half the bulk and allowed to stand. The pale yellow solid obtained thereby was designated (B) (19·0 g.) and the final mother liquor (C).

*Fraction A: Wax*

The brown insoluble solid (A) melted at about 60° and after one crystallisation from benzene-alcohol mixture (1 : 1) it was pale yellow in colour and melted at 68–75°. It was subjected to saponification as given below:

The solid (35·0 g.) was dissolved in benzene (600 c.c.), to the solution 8% alcoholic potash (100 c.c.) was added and the contents were boiled under reflux for 20 hours. Then the major bulk of the solvents was distilled off, to the concentrate purified pumice stone was added and the mixture was quickly dried to a friable mass. It was extracted in a Soxhlet, avoiding access of moisture, with dry acetone for about 20 hours, immediately followed by further extraction with dry ether for 6 hours. Both the acetone and the ether extracts were united and the solvents were removed. The crude unsaponifiable matter thus obtained was again subjected to saponification by boiling its benzene solution (300 c.c.) with 7% alcoholic potash for 8 hours. The solvents were distilled off, water was added to the residue and the aqueous suspension was subjected to repeated ether extraction. All the ether extracts were united and washed free of alkali with water. The ether solution was dried over anhydrous sodium sulphate and distilled to remove the solvent completely.

The unsaponifiable matter (20·5 g.) was brown in colour and melted indefinitely below 65°. After one crystallisation from a mixture of acetone and ether it lost most of its colour and melted between 66-75°. It was then dissolved in cold ligroin and set aside for several hours. A crystalline solid separated melting at 79–81° (10·0 g.). After three crystallisations from acetone it melted sharp at 87° and solidified at 86°. (Found: C, 82·4; H, 14·3; $C_{30}H_{62}O$ requires C, 82·2; H, 14·1%.) The acetate obtained by heating it with acetic anhydride and sodium acetate crystallised from alcohol as colourless needles and melted at 72°. Therefore this fraction sparingly soluble in ligroin consisted mostly of long-chain alcohols corresponding to the description of myricyl alcohol which has been shown by Chibnall *et al.*[5] to be a mixture of the following composition: 40% of $C_{30}$, 40% of $C_{32}$, and 20% of $C_{34}$ alcohols.

The ligroin soluble fraction (10·0 g.) was obtained by removing the solvent. It was dissolved in boiling amyl alcohol (100 c.c.), treated with an equal volume of concentrated hydrochloric acid, the mixture boiled for about 5 minutes and then allowed to cool slowly. When the temperature reached 60° a solid cake was formed at the top; it was removed and the above treatment repeated. An almost colourless solid consisting essentially of hydrocarbons resulted (7·0 g.). In order to remove the last traces of alcohols, it was dried and boiled with acetic anhydride (15 c.c.) and sodium acetate (6·0 g.) for 3 hours, the mixture was treated with a large amount of water and kept in the ice-chest. The resulting solid was treated with alcohol and acetone in succession in order to remove soluble acetates. The product (6·5 g.) was free from alcohols. (Found: C, 85·0; H, 14·5%.) It

was then dissolved in cold petroleum ether (200 c.c.) and the clear solution allowed to concentrate slowly. Six fractions were thus collected having melting points between 57° and 68°. Pairs of neighbouring fractions were united and carefully recrystallised and thus three sharp-melting solids were obtained. They were subjected to final treatment with sulphuric acid at 130° according to the method of Piper *et al.*[6] Their characteristics are given below; the melting and setting points were obtained by slow heating and cooling.

| M.P. | S.P. | Analysis | Average chain length | Probable composition |
|---|---|---|---|---|
| 68·5° | 68·0° | C, 85·3 ; H, 14·6% | $C_{31\cdot4}$ | 20% $C_{33}$+80% $C_{31}$ |
| 63·0° | 62·5° | C, 85·4 ; H, 14·4% | $C_{28\cdot6}$ | 95% $C_{29}$+5 % $C_{27}$ |
| 59·0° | 58·5° | C, 85·2 ; H, 14·7% | $C_{27\cdot8}$ | $C_{27}$ mostly |

The average chain lengths of the mixtures were obtained by reference to the curves given by Piper *et al.*[6] The probable composition of the mixtures is given only roughly by referring to the melting and setting points given by Chibnall *et al.*[5] for known mixtures of synthetic paraffins.

The soap left after the removal of the unsaponifiables was decomposed by heating with hydrochloric acid and the solid separating on the top was isolated. This was taken up in ether and washed free of mineral matter. Then the ether solution was distilled to remove the solvent; the residue (14·0 g.) melted at about 70°. It was crystallised repeatedly first from ethyl acetate and then finally from alcohol. Three fractions having sharp melting points were obtained. The average chain lengths were calculated from the molecular weights and the pobable composition of the mixture obtained by referring to the tables given by Piper *et al.*[7] relating to the melting points of known acid mixtures using synthetic compounds. Their properties and probable compositions are given below:

| | Melting point | Molecular weight by titration | Average chain length | Probable composition |
|---|---|---|---|---|
| 1. | 84·0° | 410·8 | $C_{27}$ | 20% $C_{30}$, 40% $C_{28}$ and 40% $C_{26}$ acids |
| 2. | 79·0° | 380·6 | $C_{25}$ | 20% $C_{28}$, 40% $C_{26}$ and 40% $C_{24}$ acids |
| 3. | 74·0° | 350·2 | $C_{23}$ | $C_{24}$ and immediate homologues |

*Fraction B: Wax*

It (19·0 g.) was divided into two fractions by crystallising from alcohol, benzene-alcohol mixture and finally from ether. The less soluble

fractions (5·0 g.) melted at about 86° ($B_1$) and the more soluble one ($B_2$) melted much lower (10·0 g.). Each of them was saponified separately, ($B_1$) yielded an alcohol mixture (2·2 g.) melting sharp at 87° agreeing in all respects with the $C_{30}$ alcohol mixture (myricyl alcohol) obtained in fraction (A). (Found: C, 82·1; H, 14·0; $C_{30}H_{62}O$ requires C, 82·2, H, 14·1%). The acetate crystallised as colourless needles melting at 72° (Found: C, 79·8; H, 13·6. $C_{32}H_{64}O_2$ requires C, 80·0 and H, 13·3%.) The acid fraction (2·4 g.) melted at 87° and had a molecular weight of 440·4. It therefore had an average chain length of $C_{29}$ and was probably a mixture of $C_{32}$, $C_{30}$ and $C_{28}$ acids.

($B_2$) yielded a nonsaponifiable portion part of which was a steam volatile liquid. The non-volatile portion (3·5 g.) when purified yielded a mixture of wax alcohols melting at 72–76° (Found: C, 82·1, H, 13·8%). It therefore consisted of $C_{24}$ and $C_{26}$ alcohols mostly. The fatty acid mixture (4·0 g.) contained some liquid also; it was separated by the lead salt method. The liquid acids constituted about 12%; the solid acids, when crystallised, melted at 78° and had the mean molecular weight of 375·2. This corresponded to a mixture of $C_{26}$ and $C_{24}$ acids.

*Fraction* C: *Oil, etc.*

When the alcoholic solution was concentrated to about 250 c.c. some wax separated and it was removed. On distilling the solvent completely a brown oil was obtained (38·5 g.). This was dissolved in ether (100 c.c.) and allowed to stand overnight in a refrigerator. A yellow solid (D) was deposited. It was filtered and washed with a little ether. The solution was dried over anhydrous sodium sulphate and the solvent removed under reduced pressure. The pale brown oil had the following properties: Sp. gravity 0·9321; ref. index 1·4726; acid value 39·8; sap. value 186·6; iodine value 79·2. It thus resembled the oil from the pongamia seeds[8]; no further examination was made.

*Solid* (*D*): *Pongamin*

The crude solid was recrystallised twice from boiling alcohol whereby a colourless substance (0·5 g.) was obtained in the form of long flat needles. It melted at 210–12° (decomp.). It was insoluble in water and only sparingly soluble in ether. Its solution in alcohol did not produce any colour with ferric chloride or sodium hydroxide. It dissolved in concentrated sulphuric acid to produce a yellow solution which changed to green on standing (resemblance to karanjin). Its alcoholic solution produced only a yellow colour on reduction with magnesium and hydrochloric acid and no colour by reduction with sodium amalgam. It did not give the characteristic

reactions of rotenone. (Found: C, 66·5; H, 4·8; $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4%.) The molecular weight by Rast's micromethod varied between 230 and 242; the value required for the above formula is 272.

*Ether Extract: Kæmpferol*

This was obtained as a greenish semi-solid (40·0 g.) on removing the solvent. It was boiled with alcohol (400 c.c.), the insoluble waxy matter was separated and the filtrate gradually concentrated to about a third of its bulk, the amorphous impurities that separated meanwhile being collected separately. It was then further concentrated to a syrupy consistency and allowed to crystallise. The product now melted at 252°–55°. Further crystallisation from dilute alcohol yielded a yellow needle-shaped crystalline solid melting at 274°–75° (decomp.). The yield of the pure substance was 4·0 g. Its alcohol solution gave an olive brown colour with ferric chloride and a deep yellow one with alkali. On reduction with magnesium and hydrochloric acid it developed the characteristic anthocyanin colour, deep pink. It dissolved in strong sulphuric acid exhibiting a powerful bluish green fluorescence. (Found in an air-dried sample: C, 59·5; H, 4·3 and $C_{15}H_{10}O_6$, $H_2O$ requires C, 59·2 and H, 3·9%. Loss on drying at 120° for 3 hours *in vacuo*: 6·2%; $C_{15}H_{10}O_6$, $H_2O$ requires for one $H_2O$, 5·9%.)

By acetylation using sodium acetate and acetic anhydride, a colourless acetate was obtained which crystallised from alcohol in the shape of needles. On heating it sintered and shrank markedly at 118°–20° and finally melted at 181°–182°. (Found in air-dried sample: C, 58·2; H, 3·8; $C_{23}H_{18}O_{10}$, $H_2O$ requires C, 58·5 and H, 4·2%. Loss on drying at 110° for 2½ hours *in vacuo*, 3·6%; $C_{23}H_{18}O_{10}$, $H_2O$ requires for one $H_2O$, 3·8%. Found in the sample dried at 110°: C, 60·4; H, 4·3 and $C_{23}H_{18}O_{10}$ requires C, 60·8 and H, 4·0%).

The above colour reactions and the analysis indicated that the pigment was kæmferol. This was confirmed by comparison of the substance and the acetate with authentic samples obtained from senna leaves. No depression in mixed melting points was noticed.

Though the dual melting point of the acetate was noticed long ago, there has been difference of opinion regarding the cause of it. Perkin and Wilkinson[9] believed that it was not due to solvent of crystallisation. Tutin[9] seemed to have studied the matter more closely. Employing samples crystallised from various solvents he noted that they underwent some loss when dried at 110° and the dried samples melted sharp at 183° without any previous sintering. He, therefore, concluded that some solvent of crystallisation was involved. Though he did not analyse air-dried samples for carbon and

hydrogen, the loss on drying of a sample of the acetate crystallised from ethyl acetate corresponded to the presence of half a molecule of ethyl acetate of crystallisation. From the results (C and H values) presented above it is definite that the substance crystallises from ordinary alcohol with one molecule of water of crystallisation which it loses at 110°. It is interesting to note that even kæmpferol comes as a monohydrate. In general acetates of hydroxy-flavones and -flavonols are found to be anhydrous. Kæmpferol acetate seems to be therefore an exception.

The alcohol insoluble and coloured waxy matter (8·0 g.) was dissolved in ether (500 c.c.) and extracted twice with aqueous sodium carbonate (200 c.c.) resulting in the removal of some dark slimy matter. Further extraction with 5% sodium hydroxide (6 times with 50 c.c. each time) yielded a coloured, deep red extract. From this after acidification and ether extraction some more of kæmpferol (0·8 g.) was obtained.

*Sterol*

The alkali-washed ether solution was distilled and the residue (5·0 g.) was found to consist of some waxy substance. It was hydrolysed by boiling its benzene solution with alcoholic potash for 7 hours and the non-saponifiable matter was separated by ether extraction. By repeated crystallisation a small quantity of a sterol fraction was obtained. This was acetylated by boiling with acetic anhydride and sodium acetate and the resulting product was crystallised from alcohol. It appeared as needles and rods and melted at 138–39°. On hydrolysis it yielded a sterol which on repeated crystallisation from alcohol melted at 146°. This was found to be identical with the sitosterol obtained from the phytosterolin described later.

*Alcohol Extract*

The flower powder left after ether extraction was extracted with methylated spirits (90%) in the continuous extractor for about 15 hours. By this time all the soluble components were removed; then 10% water was added to the solvent and the extraction was continued in the same apparatus for 5 more hours. By this process components that are more readily soluble in aqueous alcohol were also extracted completely. The resulting aqueous alcoholic extract was concentrated to about 800 c.c. and set aside for a week. Glistening crystals embedded in resin separated out. This was filtered and the solid (E) and the filtrate (F) were studied separately.

*Fraction E : Phytosterolin*

The solid E was washed with ether in order to remove soluble impurities and then digested with water. A portion of it dissolved forming a brown

solution. The residue was insoluble in ether, alcohol and acetone but it dissolved almost completely in boiling acetic acid or pyridine. After two crystallisations from acetic acid, it reached a constant melting point 261–62° (decomp). The yield of the pure substance was 1·2 g. With Salkowski's reagent, the chloroform layer was coloured deep red and the sulphuric acid layer exhibited a powerful green fluorescence. With the Liebermann-Burchard reagent, a pink colour was immediately produced and it rapidly changed to blue and green. (Found: C, 72·0; H, 10·6 and $C_{34}H_{58}O_6$ requires C, 72·6; H, 10·3%; $C_{35}H_{60}O_6$ requires C, 72·9, H, 10·4%.)

The sterolin was hydrolysed by boiling with amyl alcoholic hydrochloric acid and the solvent was removed by steam distillation. The residue was ether extracted and the ether solution was distilled to remove the solvent. The product was crystallised from alcohol when a crystalline sterol (needles and plates) melting at 145-46° was obtained; it formed an insoluble digitonide. (Found: C, 83·8: H, 12·3 and $C_{28}H_{48}O$ requires C, 84·0; H, 12·0%; $C_{29}H_{50}O$ requires C, 84·1; H, 12·1%.) The acetate was prepared in the usual way by boiling with acetic anhydride and sodium acetate. It crystallised as needles and rods from alcohol and melted at 138–39°.

The aqueous solution gave tests for the presence of a reducing sugar and it was identified as glucose by the preparation of the osazone. From the properties of the sterol and its acetate it appeared to be $\gamma$-sitosterol. Hence the substance melting at 261–62° may be considered to be $\gamma$-sitosterol glucoside. These three compounds were found to be identical with the sterolin, the sterol and its acetate obtained from the flowers of ***Butea frondosa*** and there was no depression in the melting points.

*Neoglabrin*

The aqueous solution obtained from (E) was decolourised with 'norit' and concentrated to about 300 c.c. on a water-bath. It was then largely diluted with alcohol (2000 c.c.) with stirring when a copious white precipitate slowly separated out. The contents were cooled in the refrigerator for 2 hours and then filtered. A shining colourless product was left on the filter and it appeared as narrow plates and rods under the microscope. It became dark red when heated to 240° and melted at 281–82° with decomposition. The yield was 0·5% on the weight of the flowers taken. It was insoluble in all solvents except water in which it readily dissolved even in the cold. It did not produce any coloured solutions either with alkali or with acid. It tasted sweet and did not have any toxic effect on fish. When boiled with acetic anhydride and sodium acetate it was completely resinified. It did not respond to Molisch's test for carbohydrates. It

contained nitrogen in addition to oxygen and hydrogen. (Found in air-dried sample: C, 38·9; H, 7·7; N, 9·9%; $C_9H_{20}N_2O_8$ requires C, 38·1; H, 7·0 and N, 9·9%. Loss on drying at 120° for 3 hours, 4·0%.) The substance was leavoratatory $(\alpha)_D^{20}$, −40·0° in water. It gave a blue copper salt and a positive nin-hydrin reaction. Thus it seemed to be an amino-acid closely allied to glabrin.[1]

*Filtrate F*: *Glabrosaponin*

The filtrate (F) was concentrated to half its bulk and allowed to stand in the ice-chest. Since no solid separated, it was treated with excess of ether so that it was saturated and a layer of ether was formed. After 2 days a brown semi-solid mixed with some crystalline matter separated. It was filtered using fluted filters and washed first with ether and then with water. Most of the colour was thus removed. The residue (20·0 g.) was then boiled with alcohol (300 c.c.) and enough water (about 100 c.c.) added so as to obtain a clear solution. On cooling the solution a colourless crystalline solid (shining hexagonal plates) separated out. It was filtered; some more quantity was obtained by concentrating the filtrate and saturating it with ether. It melted at 248–50° with decomposition. It did not dissolve completely in water but gave a turbid colloidal solution. On the addition of a small quantity of alcohol it formed a true solution. It was insoluble in ether, benzene, chloroform, etc. Its alcoholic solution did not produce any colour either with alkali or with ferric chloride. No colour was produced when it was reduced with magnesium and hydrochloric acid. It dissolved in strong sulphuric acid producing an orange-red solution changing to purple on standing. With the Liebermann-Burchard reagent it produced a purple solution. It was non-toxic to fish. There was no loss on drying the substance at 120° *in vacuo* for 3 hours. (Found in the sample dried at 120°: C, 57·2; H, 8·5 and $C_{50}H_{84}O_{23}$ requires C, 57·1, and H, 8·0%.) $(\alpha)_D^{30}$, +22·4° in aqueous alcohol.

*Hydrolysis of the Glycoside*: *Glabrosapogenin*

The crystalline solid (2·0 g.) was taken in boiling 90% alcohol (400 c.c.) and strong sulphuric acid (40 c.c.) was slowly added. The clear solution was boiled under reflux for 7 hours. Then it was largely diluted with water and boiled to remove the major bulk of the alcohol. A colourless solid soon began to separate out and the contents were kept in the refrigerator overnight. A copious crystalline solid was thus obtained and it was filtered and washed free of acid. The crude product was dissolved in alcohol (100 c.c.) and set aside. The resulting small crop of crystals melted at 193° and was removed by filtration. The mother liquor on concentration and standing

deposited a purer solid in larger amounts melting at 195–96° (needles and rods under the microscope). It did not dissolve in water but dissolved readily in boiling alcohol. It did not respond to any of the well-known sterol colour reactions but gave the characteristic colour reactions of resinols. Thus it produced a yellow solution with sulphuric acid exhibiting green fluorescence and a purple solution with the Liebermann-Burchard reagent. No colour was produced either with alkali or with ferric chloride; it did not form a precipitate with digitonin (Found: C, 72·8%; H, 10·9; $C_{30}H_{50}O_5$ requires C, 73·5 and H, 10·2%.) $(\alpha)_D^{30}$, + 72·3° in alcohol.

The aqueous acid solution obtained after hydrolysis was found to contain reducing sugars. From one portion of the solution sulphuric acid was removed by means of barium carbonate and the osazone was prepared by treatment with phenyl hydrozine hydrochloride and sodium acetate. Though it was obtained in the form of yellow needles, it melted indefinitely at about 180°. Another portion of the acid solution was carefully neutralised with aqueous sodium hydroxide and titrated against Fehling's solution. The amount of reducing sugars calculated as glucose was found to be 54·2% on the weight of the glycoside taken. The mother liquors left after separation of the saponins gave tests for the presence of small amounts of tannin.

*A Note on the Glycosidic Components of* Butea frondosa Flowers

The presence of two colourless glycosidic components in small quantities was recorded in a paper by Murti and Seshadri.[10] These have been studied in greater detail now. The dry flower petals were first extracted with ligroin in order to remove waxy matter. The fat and wax-free material was extracted with alcohol. This extract was concentrated as far as possible and treated with excess of water; a clear orange yellow solution was obtained (aqueous solution A). It was repeatedly shaken with ether in order to remove all ether-soluble portion.

*Phytosterolin*

When the ether extract was shaken with aqueous sodium bicarbonate in order to dissolve the butein-butin mixture present in it, a colourless solid separated out being insoluble both in the ether and aqueous layers. It was sparingly soluble in most solvents but could be recrystallised from glacial acetic acid or pyridine. A carefully purified sample has now been found to melt at 261–62° with decomposition. This gives the typical sterol reactions with Salkowski and Liebermann-Burchard reagents. (Found: C, 72·2; H, 10·6; $C_{34}H_{58}O_6$ requires C, 72·6; H, 10·3%; $C_{35}H_{60}O_6$ requires C, 72·9; H, 10·4%.)

The substance was hydrolysed with amyl alcoholic hydrochloric acid and the alcohol removed by steam distillation. By ether extracting the residual aqueous mixture was obtained a solid which was more easily soluble in most solvents and when finally crystallised from alcohol it melted at 145–46°. It gave the usual sterol colour reactions and formed a sparingly soluble digitonide; its acetate melted at 138–39°. The sterolin, the sterol and its acetate agreed in every respect with similar products obtained from the flowers of *Pongamia glabra*. As another product of hydrolysis the presence of glucose was established in the aqueous solution. Hence the sterolin was considered to be a glucoside of $\gamma$-sitosterol.

*Saponin*

Aqueous solution (A) that had been ether extracted was allowed to stand saturated with ether. The first crop of crystals that could be separated in the course of the first few days was pale yellow in colour and was different from butrin which separated later on. The pale yellow solid was repeatedly washed with warm water and recrystallised several times with dilute alcohol. It was then insoluble in ether and chloroform, more soluble in hot alcohol and readily soluble in pyridine and acetic acid. When recrystallised from dilute alcohol, it appeared as colourless hexagonal plates and melted at 237–38° with decomposition. Its colour reactions with Salkowski and Liebermann-Burchard reagents indicated that it belonged to the resinol group. As characteristic of all saponins it produced froth with water. (Found in a sample dried at 120°: C, 57·3; H, 8·4; $C_{50}H_{84}O_{23}$ requires C, 57·1; H, 8·0%.) In the analysis for carbon and hydrogen it resembles the saponin obtained from the flowers of *Pongamia glabra*. But the melting point of the Butea saponin is lower. This was hydrolysed by boiling with aqueous alcoholic sulphuric acid having concentration of 7% acid. After evaporating the alcohol a colourless solid was obtained. It was more easily soluble in ordinary solvents than the glycoside and on recrystallisation from alcohol it melted at 220°–22°. It gave all colour reactions of resinols and did not form a precipitate with digitonin in alcoholic solution. An air-dried sample lost 5·15% of its weight when dried at 120° for 2 hours. (Found in the oven dried sample: C, 74·9; H, 10·8; $C_{30}H_{50}O_4$ requires C, 75·9; H, 10·5%.)

Reducing sugars could be identified as other products of hydrolysis in the aqueous solution. No further data could be collected since the yield of the saponin was very small.

*Summary*

The flowers of *Pongamia glabra* have been examined in detail. The ligroin extract is made up of (1) aliphatic waxy matter, (2) some oil and

(3) a small amount of pongamin. The aliphatic waxy portion consists mostly of esters derived from $C_{24}$ to $C_{34}$ alcohols and $C_{24}$ to $C_{30}$ acids and smaller amounts (12%) of hydrocarbons of $C_{27}$ to $C_{33}$ dimensions. Pongamin is a colourless crystalline substance melting at 212° and having the approximate formula, $C_{15}H_{12}O_5$. It exhibits resemblance in properties to karanjin. The ether extract contains plenty of free kæmpferol and a small amount of γ-sitosterol occurring probably as an ester.

The alcohol extract contains small amounts of a sterolin melting at 262° and found to be γ-sitosterol glucoside. Larger amounts of neoglabrin and glabrosaponin have been found. The former is a high melting complex amino acid which is sweet in taste and resembles glabrin to a considerable extent. The glabrosaponin seems to have the formula $C_{50}H_{84}O_{23}$; it is a complex glycoside of a triterpenoid sapogenin having the probable formula, $C_{30}H_{50}O_5$.

New data are presented regarding the glycosidic components of the flowers of *Butea frondosa*. The sterolin is found to be the same as is present in the pongamia flowers. Though the butea saponin is similar being a triterpene glycoside it is not identical with glabrosaponin, neither are the aglycones the same.

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# RAMAN EFFECT IN AQUEOUS SOLUTIONS OF SOME INORGANIC GASES

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## 1. *Introduction*

Water as a solvent has been used mostly in the study of electrolytic dissociation. On the other hand the use of a solvent for working with simpler substances which do not dissociate on solution has not been very common, it being assumed that perturbations arising from the mutual interaction of solvent and solute molecules will cause difficulties.

Gerding and Nijveld[1] published a note on the study of the Raman specturm of the solution of sulphur dioxide in water. They reported that the spectrum of the solution exhibits just the same features as a gas and that there were no lines attributable to either $SO_3^{--}$ or $HSO_3^-$ ions, and concluded that a large part of the $SO_2$ molecules in the solution are present as such and that the frequency of the stronger Raman line agrees nearly with that of the gaseous $SO_2$ itself. These authors studied the solution only at one concentration and at 60°. The present investigation is undertaken in order to see if this result holds good at sufficiently higher concentrations and if so, if the relative intensities of the lines at various concentrations bear a relation to the concentration of the solution. Incidentally the effect of the solute on the structure of the Raman band in water is also studied.

The Raman spectrum of the solution of ammonia in water was first studied by Carrelli, Pringsheim and Rosen[2] and they reported frequency shifts 3314 and 3385 cm.$^{-1}$. Afterwards Hollaender and Williams[3] working with a 16 Normal solution, reported all the lines which have been previously reported from gaseous and liquid ammonia. They published a microphotometric record showing evidence of a fine structure of the vibrational band at 3 $\mu$ due to its combination with the rotation spectrum of the ammonia molecule. Later Langseth[4] working with solutions of varying concentrations and using a high dispersion instrument, was able to resolve the vibrational band corresponding to the infra-red absorption band at 3 $\mu$. Immediately after this publication, Hollaender and Williams[5] also reported almost

identical results. No new lines attributable to $NH_4^+$ ion have been reported by any of these authors. In this paper, the study of the Raman spectrum of aqueous solutions of ammonia with varying concentrations is undertaken. In this case the influence of the solute on the structure of the Raman band of water could not be studied because the vibrational Raman lines fall in the region of the water-band. The time of exposure required to record the strong Raman lines of ammonia was however short enough to avoid the difficulty due to the excitation of the water-band.

### 2. *Experimental Arrangements*

Both the gases sulphur dioxide and ammonia are taken from the commercial cylinders. The gases are rendered dust free by passing them through a series of three cotton plugs. They are finally passed into a bottle containing double distilled water. The gasses are allowed to bubble through the water at very low speed. The spectra obtained from these solutions are quite free from continuous background. The concentrations of the sulphur dioxide solutions are estimated by an iodometric method and those of ammonia solutions by standard sulphuric acid.

Light from a six-inch quartz mercury arc lamp is condensed by means of a glass condenser on to the slit of the Raman tube containing the liquid. The scattered beam is condensed by a lens on to the slit of a Fuess glass spectrograph. Raman spectra for the various concentrations are photographed on the same plate using a Hartmann diaphragm. A set of intensity marks is given on each plate by the method of varying slit widths. The plates are run through a Moll-microphotometer and the densities of the lines at various concentrations are obtained. From the density log-intensity curves drawn for each of the wave-lengths, the intensities are estimated and the ratio of the intensities of the lines at various concentrations for each of the solutions is calculated and compared with the ratio of the concentrations obtained by the volumetric method.

### 3. *Results*

Tables I and II contain the results relating to the position and ratio of the intensities of the strong Raman line in sulphur dioxide solution at different concentrations. Table III refers to the position of the water-band. Tables IV and V refer to ammonia solutions. Fig. 1 is a reproduction showing the structure of the Raman band of water at different concentrations of sulphur dioxide solutions.

TABLE I

| Gm. of $SO_2$ present in 100 c.c. of solution | Wave-length of the Raman line A.U. | Wave number of the Raman line cm.$^{-1}$ | Wave-length of the exciting line A.U. | Raman shift cm.$^{-1}$ |
|---|---|---|---|---|
| 4·7 | 4588·8 | 21786 | 4358 | 1152 |
| 4·7 | 4244·6 | 23553 | 4046 | 1152 |
| 3·3 | 4588·6 | 21787 | 4358 | 1151 |
| 3·3 | 4244·5 | 23553 | 4046 | 1152 |
| 2·3 | 4588·9 | 21786 | 4358 | 1152 |
| 2·3 | 4244·6 | 23553 | 4046 | 1152 |

TABLE II

| Gm. of $SO_2$ present in 100 c.c. of solution | Ratio of concentration calculated | Ratio of intensities observed |
|---|---|---|
| 4·7 | 2·04 | 1·90 |
| 3·3 | 1·43 | 1·35 |
| 2·3 | 1·00 | 1·00 |

TABLE III

| Wave-length in A.U. | Wave number in cm.$^{-1}$ | Wave-length of the exciting line A.U. | Components of the Raman band cm.$^{-1}$ |
|---|---|---|---|
| 4653·1 | 21485 | 4046 | 3220 |
| 4694·2 | 21297 | 4046 | 3408 |
| 4735·8 | 21110 | 4046 | 3595 |

TABLE IV

| Gm. of $NH_3$ present in 100 c.c. of solution | Wave-length of the Raman line A.U. | Wave number of the Raman line cm.$^{-1}$ | Wave-length of the exciting line A.U. | Raman shift cm.$^{-1}$ |
|---|---|---|---|---|
| 20·60 | 4672·8 | 21394 | 4046 | 3311 |
| 20·60 | 4169·1 | 23979 | 3663 | 3311 |
| 20·60 | 4158·2 | 24042 | 3654 | 3312 |
| 20·60 | 4152·1 | 24077 | 3650 | 3312 |
| 16·69 | 4673·1 | 21393 | 4046 | 3312 |
| 16·69 | 4169·2 | 23979 | 3663 | 3311 |
| 16·69 | 4158·2 | 24042 | 3654 | 3312 |
| 16·69 | 4152·2 | 24077 | 3650 | 3312 |
| 10·39 | 4672·8 | 21394 | 4046 | 3311 |
| 10·39 | 4169·1 | 23979 | 3663 | 3311 |
| 10·39 | 4158·2 | 24042 | 3654 | 3312 |
| 10·39 | 4152·2 | 24077 | 3650 | 3312 |

TABLE V

| Gm. of ammonia present in 100 c.c. of solution | Ratio of concentration calculated | Ratio of intensities observed $\Delta\nu = 3311$ |
|---|---|---|
| 20·60 | 1·98 | 1·82 |
| 16·69 | 1·61 | 1·55 |
| 10·39 | 1·00 | 1·00 |

### 4. *Discussion of the Results*

Gerding and Nijveld[1] working with gaseous sulphur dioxide at 12 atmospheres recorded the strong Raman line with a frequency shift of 1150·5 cm.$^{-1}$ whereas Bhagavantam[6] gave it as 1154 cm$^{-1}$. Table I shows that there is no change in the frequecny of the strong Raman line with the variation in concentration and the actual frequency compares well with that obtained in free gas. The spectrum shows no new lines attributable either to the $SO_3^{--}$ or $HSO_3^-$ ions. This is in conformity with the observations of Gerding and Nijveld, and shows that even at such high concentrations the solution contains a very large amount of free gas. In such a case one should expect the intensity of the Raman line to bear a relation to the population of the molecules. Table II shows that the ratios of the concentrations are in fair agreement with the ratios of the intensities of the Raman line.

The case of ammonia is similar to that of sulphur dioxide. Wood[7] and Dickinson, Dillon and Rasetti[8] worked with gaseous ammonia and recorded the frequency shift of the strong Raman line as 3309 and 3333·6 respectively. Daure,[9] Bhagavantam[10] and Dickinson, Dillon and Rasetti[8] worked with liquid ammonia and recorded the Raman shifts as 3310, 3304 and 3298 respectively. Carrelli, Pringsheim and Rosen,[2] Hollaender and Williams[3] and Langseth[4] working with solutions of ammonia in water recorded the frequency as 3311. Table IV shows that the value recorded here agrees completely with that of the previous workers and it further shows that there is no change in the frequency of the Raman line with varying concentration, a result analogous to that in sulphur dioxide. Table V shows that the concentrations of the solution are proportional to the intensities of the line.

The Raman spectrum of water has been investigated by a large number of workers and is known to consist of broad and diffuse bands extending over a range of about 500 wave-numbers. Earlier work of Rao,[11] Ganesan and Venkateswaran[12] and more recent work of Cross, Burnham and Leighton[13] show that the principal water-band consists of three definite components gradually shading into one another, the central one being the brightest. An increase in temperature causes a diminution in intensity of the

low frequency component and an increase in that of the high frequency component. The effect of solutes on the structure of the band is generally somewhat similar to that of a temperature increase. There is some difference in the interpretation given by different authors for the existence of the three components in the band. Rao has consistently ascribed the variations in the intensity of the components to a change in the relative proportions of the different possible polymers of water. According to him water at room temperature consists of $(H_2O)$, $(H_2O)_2$ and $(H_2O)_3$ molecules and the high frequency shift is ascribed to the unpolymerized water. In the present investigation the author has studied the structure of the Raman band in water excited by the mercury line 4046 A.U. in preference to that excited by 3650 A.U. group. Table III gives the three components observed in the water-band in the solutions of sulphur dioxide at different concentrations. The effect of the dissolved gas on the structure of the water-band is clearly brought out from the micro-photometric records reproduced in Fig. 1. The

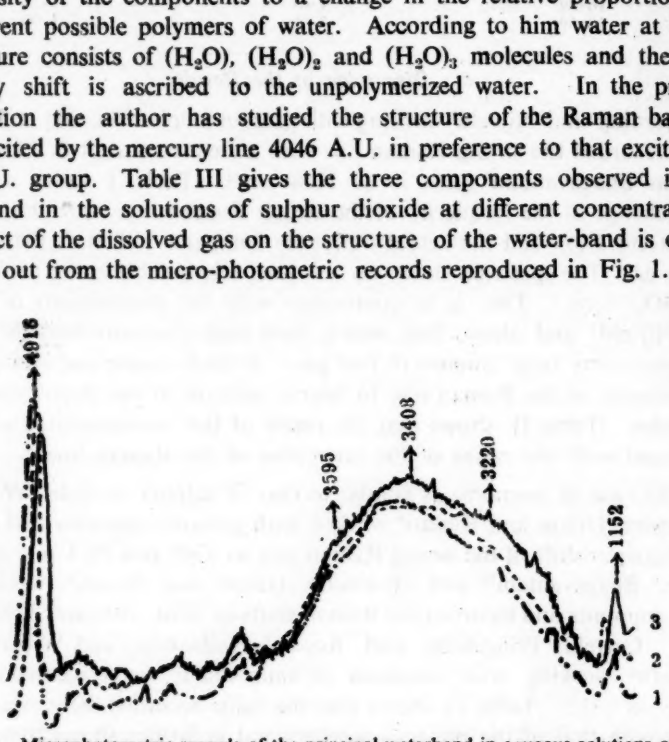


FIG. 1. Microphotometric records of the principal waterband in aqueous solutions of $SO_2$
1. 2·3% 2. 3·3% 3. 4·7%

reproduced curve shows that with increase in concentration of the solution, the low frequency components $\Delta\nu = 3220$ cm.$^{-1}$ and $\Delta\nu = 3408$ cm.$^{-1}$ increase in intensity while the intensity of the high frequency component $\Delta\nu = 3595$ cm.$^{-1}$ does not show any marked variation. This result is very interesting in that the effect of the gaseous solute studied here seems to be different from the effects of the solutes studied by the earlier authors on the structure of the Raman band for water. It may be mentioned that the molecules of both the solute and the solvent used in this particular investigation are highly polar and this may be partly responsible for the abnormal result recorded.

It is not easy to fit the observation recorded here with the idea of depolymerization with increasing concentration of the solute molecules.

## 5. *Summary*

The Raman spectra of the solutions of sulphur dioxide and ammonia in water at different concentrations are recorded using a Hartmann diaphragm and it is found that there is no shift in the frequency of the strong Raman line in both the solutions with changing concentration. No new lines attributable to $SO_3^{--}$ or $HSO^-_3$ or $NH_4^-$ ions could be recorded. It is also observed that the ratios of the concentrations of the solutions in both the cases are equal to the ratios of the intensities of the lines. Further it is observed that the intensities of the low-frequency components of the water-band in the solution of sulphur dioxide tend to increase in comparison to that of the high frequency component with increasing concentration.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam under whose guidance the present investigation has been carried out.

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# ELASTIC CONSTANTS OF CRYSTALS

## A New Method and Its Application to Pyrites and Galena

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### 1. *Introduction*

In a recent note we reported[1] on a new method for the determination of the elastic constants of crystals. The purpose of the present paper is to explain in detail the new method and apply it to the cases of Pyrites and Galena which crystallise in the cubic system.

A review of the literature shows that there are a number of different experimental methods by which the elastic constants of crystals can be determined. The first of these is the well-known static method due to Voigt.[2] By bending and twisting crystal plates of different orientations, Voigt has obtained the complete set of elastic coefficients (the S's) that characterise the given crystal. The elastic constants (the C's) are then calculated from the relations that exist between the C's and the S's.

Bergmann and others[3] have developed a dynamical method. The transparent crystal is usually taken in the form of a cube, cut and polished with one of its edges parallel to a crystallographic axis. This is then cemented to a quartz oscillator. The quartz is set to vibrate at one or the other of its overtones, and thus the crystal cube is thrown into resonant vibrations. This sets up a three-dimensional ultra-sonic grating in the crystal and a beam of light passing through it shows the cross-grating effects. Knowing one of the elastic constants, all the others can be calculated from these patterns. They have also developed a method which is applicable to opaque crystals. The patterns in such cases are obtained by reflection at a surface. Difficulties of interpretation have restricted the use of the latter method.

Atanasoff and Hart[4] and Suryanarayana[5] have developed another method which is applicable only to piezo-electric crystals. Plates of known orientation are cut from the mother crystal and are set into vibration piezo-electrically. The observed modes are identified with those required by Christoffel's theory and hence the elastic constants are calculated. This method yields results which are probably subject to various corrections as shown by Lawson.[6]

Baumgardt[7] has developed a fourth method. Crystal plates of known orientation and having different thicknesses are placed in the path of a supersonic beam and the acoustical energy which penetrates through the plates is measured by a torsion balance. The position of maximum transparency is thus located and used to calculate the elastic constants.

The method of composite piezo-electric oscillator developed by Balamuth[8] has yielded very good results for single crystals of metals and other substances. To a rectangular plate of piezo-quartz is cemented a long specimen of the material of known orientation and having very nearly the same cross-section as the quartz. The composite body is suspended by fine threads. A loosely coupled oscillator is used to drive the composite block. Resonance frequencies are detected by using a thermo-microammeter. Knowing the resonance frequency of the quartz alone and those of the compsite block, the elastic constants of the specimen are calculated from observations on a requisite number of crystal plates. This method has also been used to determine the variation of the elastic constants with temperature.

### 2. *Description of the Method Used in the Present Investigation*

In these experiments a suitably cut and silvered quartz or tourmaline wedge is used as a piezo-electric vibrator. A series fed Hartley oscillator using a Mullard D. O. 24 tube serves as the source of excitation. As the frequency of the electrical circuit is varied, different points on the wedge are thrown into resonance and thus give a continuous ultrasonic spectrum. The range of the spectrum depends upon the angle of the wedge. Different wedges have been used in our investigations. A particular wedge of tourmaline covering a range of 2 to 10 MCs. has been found to be very useful.

The crystal plate is placed on an annular brass electrode. The wedge is laid on the crystal, using some liquid for securing good acoustical contact. The top of the wedge is touched lightly by a spring which keeps the wedge and the crystal pressed on to the brass electrode. This spring also functions as the second electrode. The mount is provided with levelling screws to facilitate accurate alignment. The arrangement is then dipped into a trough containing carbon tetrachloride. The ultrasonic beam from the wedge passes through the crystal and then enters the liquid. A beam of light with the usual optical arrangements is made to pass through the ultrasonic grating in the liquid and the Debye-Sears diffraction effects are observed. When the frequency of the wedge corresponds to the fundamental or an overtone of the thickness longitudinal vibration of the plate, the sound beam is best transmitted and the Debye-Sears pattern will have the maximum intensity.

It has been found that the setting for maximum transparency is very sharp and is capable of being reset to within 1 or 2%. The transmission frequency is then measured with a Philips Heterodyne Wavemeter.

With the observed value of the fundamental frequency $f$ and the measured thickenss $d$, the velocity $v$ of propagation of longitudinal sound waves, in a direction parallel to the thickness of the plate, is calculated from the relation $v = 2df$. Using this value of $v$ in Christoffel's equations, the effective elastic constant $C'_{33}$ for the plate is calculated* from the relation $C'_{33} = v^2\rho$. $\rho$ is the density of the material of the plate.

This method will not permit us to transmit thickness transverse waves and so has necessarily to be supplemented by at least one static torsion experiment if we desire to obtain the full set of elastic constants. For this purpose, the usual Searle's torsion apparatus for wires is modified for use with crystals in the present investigation. The twist is measured by using two mirros mounted on the crystal plate, and a lamp and scale arrangement. A great degree of accuracy is obtained by measuring the shift of the light spot with a travelling microscope. Voigt has shown that when a crystal plate with its length parallel to a trigonal or higher order axis, or a digonal axis perpendicular to a second digonal axis, or perpendicular to a symmetry plane is twisted, the twist $\theta$ is given by

$$\theta = \frac{3\,MlS'_{55}}{bd^3\,16\,(1-0{\cdot}63d/b)}$$

where $l$ is the length, $2b$ is the breadth and $2d$ is the thickness of the plate. M is the twisting couple. In the case of plates of cubic crystals with lengths parallel to a cube edge $S'_{55} = S'_{44} = S_{44} = \frac{1}{C_{44}}$. To apply the above formula it is essential that $b > 3d$. In selecting plates, these facts are borne in mind.

### 3. *Results of Check Experiments on Aluminium*

In a series of check experiments, plates of commercial aluminium cut and ground have been used. For a plate of thickness 1·58 mm. maximum transmission occurred at 2·092 MCs. which gives a value of $11{\cdot}80 \times 10^{11}$ dynes per sq.cm.† for the elastic constant $C_{11}$ of aluminium. It may be remarked here that transmissions at overtone frequencies of 4·183 MCs. and 6·25 MCs. have also been observed for the same plate. For the static experiments on torsion, a plate about 2 cm. long, 4 mm. broad and 1 mm.

* For an account of Christoffel's theory and the values of $C'_{33}$ in specific cases, see a following paper by Bhagavantam and Suryanarayana published in this number.

† In this and subsequent papers the elastic constants will be given in units of $10^{11}$ dynes per sq.cm.

thick was used and an average value of 2·55 was obtained for $C_{44}$. Treating the plate as an isotropic substance, and using the relation between the Youngs modulus and the constants $C_{11}$ and $C_{44}$, a value of 6·95 is obtained for the Youngs modulus of aluminium. This may be compared with 7·05 which is the usually accepted value.

### 4. *Elastic Constants of Pyrites*

Pyrites crystallises in the cubic system and belongs to the class $T_h$. Its elastic constants have already been measured by Voigt by static methods. According to Voigt this crystal has a negative $C_{12}$. This has been attributed by some workers[9] to a possible existence of twinning in the plates used by him.

Flawless single cubes of Pyrites obtained from Nepal and kindly supplied to us by Sir. C. V. Raman have been used in these investigations. Sections parallel to (100) and (110) faces have been cut and ground. A (100) plate of 0·96 mm. thickness showed a transmission fundamental at 4·42 MCs. giving an effective constant $C_{33}' = C_{11} = 36·2$. A transmission on (110) of 0·98 mm. thickness showed a fundamental at 3·69 MCs. giving an effective elastic constant $C_{33}' = \frac{1}{2}(C_{11} + C_{12} + 2C_{44}) = 26·3$. In both these cases, the results represent averages of a number of readings taken. In the static torsion experiment with a (100) plate, $C_{44}$ has been obtained as 10·4. Combining these results, we get $C_{12}$ as $-4·4$. The elastic constants thus obtained by us are compared in Table I with those of Voigt.

TABLE I

*Elastic Constants of Pyrites*

| | Authors | Voigt |
|---|---|---|
| $C_{11}$ | 36·2 | 36·1 |
| $C_{12}$ | −4·4 | −4·74 |
| $C_{44}$ | 10·4 | 10·54 |

### 5. *Elastic Constants of Galena*

Galena belongs to the $O_h$ class of the cubic system. A single cube obtained from Cherokee County, Kansas, U.S.A., has been used in these investigations. Elastic constants of Galena have not been measured so far by anyone. Hence a large number of sections have been prepared and used during the present investigations and fuller details of the results are given.

TABLE II

*Measurements on Galena*

| Plate | Thickness in mm. | Density | Transmission fundamental frequency in MCs. | Effective Elastic Constant $C_{33}'$ | |
|---|---|---|---|---|---|
| | | | | Value | Expression |
| (100) | 0·41 | 7·564 | 2·265 | 2·61 | $C_{11}$ |
| (100) | 1·96 | 7·564 | 0·486 | 2·75 | $C_{11}$ |
| (100) | 2·44 | 7·564 | 0·379 | 2·59 | $C_{11}$ |
| (110) | 1·56 | 7·560 | 1·124 | 9·29 | $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ |
| (111) | 1·48 | 7·565 | 1·328 | 11·69 | $(1/3)(C_{11}+2C_{12}+4C_{44})$ |
| (210) | 1·47 | 7·563 | 1·033 | 6·98 | $(1/25)(17C_{11}+8C_{12}+16C_{44})$ |

For the static torsion experiments, a (100) plate 1·98 mm. thick and 6·23 mm. broad and about 7 mm. long was used. The length of the plate is parallel to a cube edge. The bobbin used for applying the couple had a diameter of 1·93 cm. When the effective length under torsion was 5·20 mm. the twists oberved for different loads are given below.

TABLE III

*Twisting of a Galena Plate*

| Load in gm. .. .. .. | 20 | 40 | 60 |
|---|---|---|---|
| Twist in $10^{-5}$ radians .. .. | 3·48 | 6·52 | 10·43 |

Average twist for 20 gms. load is $3·41 \times 10^{-5}$ radians. This gives us a value of $C_{44} = 4·39$. When the effective length under torsion was 5·25 mm. and the load was 50 gms. the twist was $8·48 \times 10^{-5}$ radians giving a value of $C_{44} = 4·54$. The average of these two gives a $C_{44}$ of 4·47.

Measurements on (100) give an average value of 2·65 for $C_{11}$ (Table II). Combining with the observations on (110), we get a value of 6·99 for $C_{12}$. The three elastic constants are therefore obtained as $C_{11} = 2·65$; $C_{12} = 6·99$; $C_{44} = 4·47$.

The transmissions on (111) and (210) are used as checks. The effective constants $C_{33}'$ calculated by assuming the above values come out as 11·50 and 6·88 for the (111) and (210) plates respectively. These compare very well with the observed figures 11·69 and 6·98.

### 6. *Discussion of Results*

So far as the results on Pyrites are concerned, we confirm the observations of Voigt. The negative value of $C_{12}$ cannot presumably be

attributed to twinning. Another interesting feature of Pyrites is the complete breakdown of Cauchy's relations.

In the case of Galena, there are again two noteworthy features. The first is the breakdown of Cauchy's relations and the second is the surprisingly low value of $C_{11}$, which is perhaps connected with the easy cleavage along (100).

The observed values of the elastic constants enable us to calculate the bulk modulus $K = (\frac{1}{3})(C_{11} + 2C_{12})$ for Galena which comes out as 5·44 comparing very well with 5·11 due to Madelung and Fuchs.[10]

## 7. *Summary*

A new method for determining the elastic constants of crystals based on the transmission of longitudinal sound waves is given. The novelty of the method consists in the use of a continuous ultrasonic spectrum and the employment of the Debye-Sears effect as a delicate test for detecting maximum transmission. The method needs to be supplemented by at least one static torsion experiment to obtain the complete system of elastic constants. It has been applied to the cases of Pyrites and Galena. Voigt's results on Pyrites are confirmed and values for the elastic constants of Galena are given for the first time.

One of us (J.B.) takes this opportunity to express his thanks to the authorities of the Andhra University for the award of the Raman Scholarship enabling him to carry out research work in the Andhra University.

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# ELASTIC CONSTANTS OF PIEZO-ELECTRIC CRYSTALS

## Zinc Sulphide

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### *1. Introduction*

Atanasoff and Hart[1] evolved a method of determining the elastic constants of piezo-electric crystals. These authors directly measured the frequencies of piezo-electric vibration of plates of known orientation cut from the mother crystal. Since such frequencies are related to the elastic constants, the latter are easily evaluated if data regarding a sufficient number of plates is available. The plates were made to vibrate piezo-electrically as a filter between a variable frequency, stable oscillator and a vacuum tube volt-meter for detecting resonance frequencies of the plates. The case of quartz has been dealt with by them in this manner.

Diffraction of light by ultrasonic waves set up in liquids observed first in 1932 by Lucas and Biquard[2] and by Debye and Sears[3] provides us with a new and delicate method of detecting the resonance frequencies of a piezo-electrically vibrating crystal plate. X-cut quartz plates are now frequently used for setting up ultrasonic waves in liquids and a considerable literature has grown around this subject. The present authors have, however, found that a suitably cut crystal plate of any piezo-electric material such as zinc blende or tourmaline can be just as successfully employed in such investigations. In all such cases, the appearance of diffraction fringes in the usual arrangement can be taken as a delicate test for detecting the resonance frequencies of the plate under investigation. If the resonance frequencies of a sufficient number of differently oriented plates in a given crystal are thus detected and measured, the elastic constants may be calculated.

The above statements apply generally to all classes of piezo-electric crystals but in this paper, only the cubic system is dealt with and zinc sulphide belonging to the tetrahedral group of the cubic system ($T_D$ class) is investigated in detail. This is a typical example of piezo-electric substances crystallising in the cubic system.

### *2. Propagation of Sound Waves Along a General Direction in a Cubic Crystal*

In general, a sound wave travelling along a particular direction within a crystal can have three different velocities. The mathematical relationships

existing between the elastic constants and the velocities of propagation of waves along different directions in such cases have been known for many years.[4] The theory, however, is applicable only to infinite plates and we shall first state the important results. The following determinantal equation gives three real positive roots for $v^2$ for a given set of values $l$, $m$, $n$ and these three roots represent the squares of the three possible velocities for a sound wave travelling in the direction $l$, $m$, $n$ in the crystal.

$$\begin{vmatrix} \lambda_{11}-\rho v^2 & \lambda_{12} & \lambda_{31} \\ \lambda_{12} & \lambda_{22}-\rho v^2 & \lambda_{23} \\ \lambda_{31} & \lambda_{23} & \lambda_{33}-\rho v^2 \end{vmatrix} = 0$$

$l,m,n$ are the direction cosines of the axis along which the sound wave is travelling and $\lambda$'s are given by the following equations:—

$$\lambda_{11} = C_{11}l^2 + C_{66}m^2 + C_{55}n^2 + 2C_{56}mn + 2C_{15}nl + 2C_{16}lm$$

$$\lambda_{12} = C_{16}l^2 + C_{26}m^2 + C_{45}n^2 + (C_{46}+C_{25})mn + (C_{14}+C_{56})nl + (C_{12}+C_{66})lm$$

$$\lambda_{31} = C_{15}l^2 + C_{46}m^2 + C_{35}n^2 + (C_{45}+C_{36})mn + (C_{13}+C_{55})nl + (C_{14}+C_{56})lm$$

$$\lambda_{22} = C_{66}l^2 + C_{22}m^2 + C_{44}n^2 + 2C_{24}mn + 2C_{46}nl + 2C_{26}lm$$

$$\lambda_{23} = C_{56}l^2 + C_{24}m^2 + C_{34}n^2 + (C_{44}+C_{23})mn + (C_{45}+C_{36})nl + (C_{46}+C_{25})lm$$

$$\lambda_{33} = C_{55}l^2 + C_{44}m^2 + C_{33}n^2 + 2C_{34}mn + 2C_{35}nl + 2C_{45}lm$$

The C's in these equations are the elastic constants. In the case of a cubic crystal, there are only three independent constants given by $C_{11}=C_{22}=C_{33}$ and $C_{12}=C_{13}=C_{23}$ and $C_{44}=C_{55}=C_{66}$, all others vanishing. The determinant then takes the following simple form:

$$\begin{vmatrix} C_{11}l^2+C_{44}(m^2+n^2)-\rho v^2 & (C_{12}+C_{44})lm & (C_{12}+C_{44})ln \\ (C_{12}+C_{44})ml & C_{11}m^2+C_{44}(l^2+n^2)-\rho v^2 & (C_{12}+C_{44})mn \\ (C_{12}+C_{44})nl & (C_{12}+C_{44})nm & C_{11}n^2+C_{44}(l^2+m^2)-\rho v^2 \end{vmatrix} = 0$$

The determinant may be further simplified if specific directions are considered. The roots obtained in three special cases in all of which the determinant splits into three linear equations, are given below. $\rho$ is the density of the medium.

| Propagation of the wave along | $l, m, n$ | $v_1^2\rho$ | $v_2^2\rho$ | $v_3^2\rho$ |
|---|---|---|---|---|
| [001] axis | 0, 0, 1 | $C_{11}$ | $C_{44}$ | $C_{44}$ |
| [111] axis | $\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}$ | $\frac{C_{11}+2C_{12}+4C_{44}}{3}$ | $\frac{C_{11}-C_{12}+C_{44}}{3}$ | $\frac{C_{11}-C_{12}+C_{44}}{3}$ |
| [011] axis | $0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}$ | $\frac{C_{11}+C_{12}+2C_{44}}{2}$ | $C_{44}$ | $\frac{C_{11}-C_{12}}{2}$ |

The root occurring under $v_1^2\rho$ in each case represents the longitudinal vibration and those under $v_2^2\rho$ and $v_3^2\rho$ represent the transverse vibrations. In the case of cubic crystals, it is easy to cut plates which are parallel to various crystallographic faces and it has been found that in such cases, the manner of excitation and detection adopted in this investigation enables us to deal with only the thickness longitudinal vibrations. From the measured velocities of such vibrations, the effective elastic constants appropriate to the plates chosen can be calculated. In the case of a cubic crystal, there appear, however, certain special difficulties as two of the three plates enumerated above are not piezo-electrically excitable. Thus independent measurements have also to be made by employing static and other methods before values of reasonable accuracy can be arrived at.

### 3. *Experimental Arrangements*

A crystal of zinc sulphide* showing clearly defined and well developed faces is chosen and a number of sections parallel respectively to the 001, 111, 011 and 221 planes are cut and ground to uniform thickness. Care is taken to see that the specimen chosen does not exhibit twinning. The plates used in the present investigation are a few centimeters in length and breadth and less than two millimeters in thickness. Errors due to finite size are thus minimised. The faces in each case are silvered in the usual manner and the plate is made to oscillate by applying an alternating electric field, obtained from a Hartley Oscillator circuit. The crystal holder is so made that one of the faces of the crystal can be brought into contact with the surface of a liquid like carbon tetrachloride or water contained in a cubical vessel as in experiments designed to study the diffraction of light by stationary ultrasonic waves in liquids. As the variable capacity in the oscillatory circuit is continuously altered, positions where the diffraction patterns are clearly

* Chemical analysis of the sample used gives the following results: Moisture 0·075%; $SiO_2$ 2·155%; $Fe_2O_3+Al_2O_3$ 3·74%; Cu 1·03%; ZnS 93·64%. We are indebted to Mr. D. Venkateswarlu for this analysis.

seen may easily be picked out and identified as positions at which the crystal plate is oscillating in resonance with the oscillator and communicating its oscillations to the liquid. The frequencies at all such positions are measured with a standard heterodyne wave-meter and the corresponding velocities obtained by multiplying the frequency with twice the thickness of the plate or fractions thereof according as the crystal plate is oscillating in its fundamental or in one of its harmonics. The thickness and density of the plate under investigation are measured separately. With a given plate, a number of frequency readings are usually taken and the average obtained for deriving the elastic constants.

### 4. *Piezo-Electric Properties of Zinc Sulphide*

There is only one piezo-electric constant in the case of cubic crystals and this may be designated as $e_{14}$ in Voigt's notation.[5] The components of strain will be related to the components of piezo-electric moment in accordance with the relationships

$$P_x = e_{14} \cdot yz; \qquad P_y = e_{14} \cdot xz; \qquad P_z = e_{14} \cdot xy.$$

It may now be shown that in the case of the 001 and the 110 plates, an electric moment applied along the axis normal to the plates will only cause strong tangential strains which by their very nature are incapable of being communicated to the liquid. In agreement with this expectation, we are unable to obtain any diffraction patterns for these two sections. An electric moment so applied in the case of the 111 and 221 plates will cause strong longitudinal strains. In the case of the 111 plates, the longitudinal effect is indeed found to be very strong as is to be expected from the theory. The result obtained from the 221 plate in this manner also refers to the longitudinal effect but may not be used to give independent results as it differs only by a small amount from that of the 111 section on account of certain special conditions that exist in this crystal. It has accordingly been employed for furnishing an additional check.

In deriving the constants themselves, the value obtained for $v_1^2 \rho$ in respect of the 111 plate is combined with two other observations. A special transmission method, designed in this laboratory and described in the previous paper[6] enables us to obtain $C_{11}$ from a 001 plate. The usual static torsion method† enables us to obtain $C_{44}$ by working on a plate, the length of which is parallel to a cube edge. The third constant $C_{12}$ is obtained by elimination. As has already been mentioned, the effective elastic constants

† This method is based on principles of static torsion applicable to plates. Details are given in the foregoing paper.

obtained by employing the piezo-electric method of this paper in respect of the 221 section and the transmission method in respect of the 110 section are used as additional checks.

### 5. *Results*

The following table gives the results:

TABLE I

*Elastic Constants of Zinc Sulphide*

| Plate | Thickness cm. | Density gm. per c.c. | Observed fundamental Mc. per sec. | Identification of the mode | Method employed | Elastic constant dynes per sq. cm. |
|---|---|---|---|---|---|---|
| 001 | 0·102 | 4·109 | 2·512 | Thickness Longitudinal | Transmission | $C_{11} = 10{\cdot}79 \times 10^{11}$ |
| 111 | 0·197 | 4·078 | 1·481 | ,, | Piezo-electric | $\frac{C_{11}+2C_{12}+4C_{44}}{3} = 13{\cdot}90 \times 10^{11}$ |
| 110 | 0·102 | 4·061 | 2·790 | ,, | Transmission | $\frac{C_{11}+C_{12}+2C_{44}}{2} = 13{\cdot}15 \times 10^{11}$ |
| 221* | 0·1936 | 4·078 | 1·493 | ,, | Piezo-electric | $\frac{11C_{11}+16C_{12}+32C_{44}}{27} = 13{\cdot}64 \times 10^{11}$ |

* In this case, the cubic does not split into linear equations. The effective elastic constant given corresponds approximately to the observed longitudinal velocity.

Combining the first two results with the result $C_{44} = 4{\cdot}12 \times 10^{11}$ determined in this laboratory by the static torsion method, we obtain

$$C_{11} = 10{\cdot}79 \times 10^{11}; \quad C_{12} = 7{\cdot}22 \times 10^{11}; \quad C_{44} = 4{\cdot}12 \times 10^{11}.$$

If these values are substituted for the constants in respect of 110 section, we obtain $13{\cdot}13 \times 10^{11}$ which checks very well with the observed result. If they are substituted for the constants in respect of 221 section, we obtain $13{\cdot}56 \times 10^{11}$ which checks well with the observed result.

### 6. *Discussion of Results*

The elastic constants given in this paper lead to a bulk modulus of zinc blende $K = (C_{11} + 2C_{12})/3 = 8{\cdot}41 \times 10^{11}$ dynes per sq. cm. which may be compared with the figure of $7{\cdot}66 \times 10^{11}$ available in the literature.[7] Voigt[8] determined the elastic constants of zinc blende by static methods and obtained the following values:

$$C_{11} = 9{\cdot}43 \times 10^{11}; \quad C_{12} = 5{\cdot}68 \times 10^{11}; \quad C_{44} = 4{\cdot}37 \times 10^{11}.$$

There is agreement in the order of magnitude between these results and those obtained by us. The approximate equality of $C_{11}$ and $C_{12}+C_{44}$ may be noted[9].

## 7. *Summary*

An experimental method of detecting and measuring the resonance frequencies of piezo-electric crystal plates is described. The elastic constants of zinc blende have been obtained by this method as $C_{11}=10{\cdot}79\times10^{11}$; $C_{12}=7{\cdot}22\times10^{11}$ and $C_{44}=4{\cdot}12\times10^{11}$ dynes per sq. cm.

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